# MEMOIRS

AND

# PROCEEDINGS

OF THE

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OF

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FOR

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# MEMOIRS

AND

# PROCEEDINGS

OF

# THE CHEMICAL SOCIETY.

November 3, 1845.—The President, Prof. Graham, in the Chair.

The following presents to the Library and Museum of the Society were announced :—

Monographs and Memoirs by Dr. Alex. Petzholdt: "Über Calamiten und Steinkohlenbildung," "De Calamitis et Lithonthracibus," "Additamenta ad Saxoniæ Palæologiam," "Versuch einer neuen Gletschertheorie," "Die Galvanische Vergeldung, Versilberung, Verkupferung, u. s. w.," "Beiträge zur Naturgeschichte des Diamantes," "Beiträge zur Geognosie von Tyrol," "Populäre Vorlesungen über Agricultenchemie," and "Geology," presented by the author.

By W. Haidinger: "Über den durchsichtigen Andalusit von Minas novas in Brasilien und den Diaspor von Schemnitz," "Über die Pseudomorphism," "Über den Pleochroismus der Krystalle," 10 copies of each presented by the author for distribution.

By Dr J. Roth: "Die Kugelformen im Mineralreiche und deren einfluss auf die Absonderungsgestalten der Gesteine," from the author.

"Notice sur la vie et les écrits de Théodore de Saussure, par M. le Professeur Macaire," from the author.

"The Second Report of the Health of Towns Commission," two volumes.

"Notices of some Agricultural Analyses made by Students in the Glasgow University Laboratory," from Dr. R. D. Thomson.

A specimen of Brown Hematite from Morocco, presented by W. J. Cock, Esq.

A specimen of crystallized Copper from a fissure in an old refining furnace, by Mr. S. Piesse.

Portions of Candles converted into Stearate of Lime, from the lead mines of Derbyshire, by W. Lucas, Esq.

Thomas Hughes, Esq., and J. C. Nesbitt, Esq., were elected members of the Society (May 19th).

The following papers were read:—

Notice by Mr. S. Piesse on certain Impurities in Commercial Sulphate of Copper.

One source of the sulphate of copper of commerce is the treatment of brass and German silver articles technically called dipping, which consists in plunging them for a short time into a mixture of nitric and sulphuric acids, an operation which removes the coat of oxide from the surface of the metal, and leaves the latter in a clean state proper for the reception of varnish or other finishing. In time this dipping liquid becomes in great measure saturated, and after neutralization with old copper yields on evaporation in leaden pans a large quantity of sulphate of copper in crystals. According to the author not less than 100 tons of dipping liquid are thus disposed of annually at Birmingham by the makers of buttons and other articles. The crystallized sulphate of copper so obtained is often largely contaminated with sulphate of zinc, which may sometimes be seen in the form of slender white needles on the surface of the dark blue crystals, and in some of the applications of this salt may prove injurious. Sulphate of nickel, sulphate of lead, arsenic, and chlorides are also sometimes present.

## CXLIX. *On the relation of Ozone to Hyponitric Acid.* *By* Dr. C. F. Schœnbein.

THE chemical effects produced by atmospheric air charged with hyponitric acid ($NO_4$) are so very like those caused by ozonized air, that some chemists are inclined to consider hyponitric acid as identical with ozone. Both decompose iodide of potassium, transform the yellow prussiate of potash into the red one, decompose sulphuretted hydrogen, colour blue the resin of guaiacum, destroy organic colouring matters, polarize negatively platinum, &c.

In spite of the similarity of chemical properties exhibited by ozone and hyponitric acid, those substances are in many other respects so entirely different that their being identical cannot be thought of: thus ozone is produced under circumstances in which an essential constituent part of hyponitric acid is absent, namely nitrogen. The analogy existing between the chemical action of the two bodies mentioned appears however so striking, that we can hardly help suspecting some connexion to exist between them, and with the view of ascertaining that connexion I have of late made many experiments the account of which will form the substance of this paper.

The results obtained from these researches are, in my opinion, such as to speak strongly in favour of my conjecture that there exists a compound composed of $NO_2 + HO_2$. It

appears to me probable that besides hydrate of nitric acid a peroxide of azote and hydrogen is formed when water acts upon hyponitric acid. Agreeably to my view, the presence of $NO_2 + HO_2$, in the acid mixture, is the cause why the latter decomposes iodide of potassium, &c.

I think it cannot be denied that aqueous vapour will act upon vaporous hyponitric acid as liquid water does upon the liquid acid. Such being the case, and supposing that in the latter case two compounds of the formulas $NO_4 + HO_2$ and $NO_2 + HO_2$ are produced, it must then be admitted also that the same compounds are formed when the vapours of hyponitric acid are mixed with moist atmospheric air. Now if the peroxide of azote and hydrogen (the first of these compounds) should happen to be a volatile substance, it follows further that in a bottle containing moist air, to which vapour of hyponitric acid had been added, an atmosphere must be produced containing some $NO_2 + HO_2$, and possessing the property of causing the reactions above mentioned. The peroxide of hydrogen contained in $NO_2 + HO_2$ would be the oxidizing agent, decomposing *e. g.* iodide of potassium, &c.

For various reasons I am inclined to consider ozone as $HO_2$, *i. e.* a compound isomeric with Thenard's peroxide of hydrogen. Now if this conjecture should be true, and if there should exist a compound of $NO_2 + HO_2$, moist atmospheric air being charged with vapour of hyponitric acid would owe its reactions to the presence of ozone. How far such a conjecture is founded upon facts, the experiments I am about to detail will show.

If a piece of carbonate of ammonia, having been strongly ozonized by the means of phosphorus, is suspended in atmospheric air until the latter be so charged with ammoniacal vapours as rapidly to restore the blue colour of reddened litmus paper, that atmosphere continues to enjoy bleaching powers, decomposes iodide of potassium, colours blue the paste of starch containing that salt, transforms the yellow prussiate of potash into the red one, colours the resin of guaiacum blue, discharges the colour of sulphuret of lead; continues, in one word, to possess all the properties belonging to ozone. Hence it follows that ozone is capable of co-existing with the vapours of carbonate of ammonia without suffering decomposition; and I have ascertained that pure ammonia also does not perceptibly destroy ozone. Now if there exists $NO_2 + HO_2$, we may presume from its constitution that it will likewise be able to coexist with the vapours of the carbonate of ammonia, $NO_2$ being of itself inactive towards ammonia.

Hyponitric acid, or red fuming nitric acid, was gradually mixed up with so much water as to obtain a colourless liquid.

The bottom of a spacious bottle was covered with this mixture, and then a large piece of carbonate of ammonia suspended within the vessel. After the atmosphere, standing over the acid liquid, had assumed the power of colouring rapidly blue a strip of reddened litmus paper, it continued to possess the following properties:—

1. Strips of paper charged with paste of starch containing some iodide of potassium were coloured blue.
2. Strips of paper drenched with an alcoholic solution of guaiacum assumed a blue colour.
3. Strips of paper coloured blue by a solution of indigo turned white.
4. Strips of paper to which sulphuret of lead had been attached, by means of nitrate of lead and sulphuretted hydrogen, gradually turned white.
5. Strips of paper charged with a solution of the common prussiate of potash became deeply yellow.
6. Crystals of the yellow prussiate, after having been suspended for twenty-four hours within this atmosphere, were covered with a crust of the red sesqui-ferrocyanuret of potassium.

From the facts just stated, it appears that the atmosphere in question acts exactly in the same way as ozonized air does, and from the circumstances under which those reactions took place, it follows that the latter could not proceed from free hyponitric or nitrous acid, these acids not being able to coexist in a state of isolation with the vapours of carbonate of ammonia. We must therefore conclude from these facts, that there was a principle present, in the atmosphere mentioned, which acted after the manner of ozone, and conducted itself, in spite of the presence of ammoniacal vapour, as a highly oxidizing agent.

But if neither free hyponitric nor nitrous acid were the cause of the reactions mentioned, nor nitrite of ammonia, what then is the substance to which the oxidizing powers are to be ascribed? I can answer that question only by supposing that the peroxide of azote and hydrogen is that agent. Before passing to another subject, I take the liberty to mention a circumstance which seems to bear upon the matter in question, and merit some attention. On breathing strongly ozonized air three or four times, a disagreeable and strangling sensation will be experienced near the throat and in the chest. This sensation is very similar to that caused by inhaling air which has stood for some time over a mixture of hyponitric acid and water, and this is the case even if the air happens to be charged with ammoniacal vapours. We observe also in such an atmosphere a peculiar and disagreeable odour,

which is similar to that of common aquafortis, and slightly analogous to the smell of chlorine. It is likely that the odour mentioned belongs to the vapour of our supposed peroxide of azote and hydrogen, and that it is *that* compound which, if inhaled, causes the sensation before mentioned. With regard to the subject under discussion, it seems to me that the way in which the mixture, formed from hyponitric acid and water, acts upon a solution of the yellow prussiate of potash, offers peculiar interest.

My experiments having demonstrated that the salt just mentioned (be it solid or dissolved in water) is readily transformed into the red cyanuret by ozone, and considering the acid mixture before alluded to as an aqueous solution of nitric acid and peroxide of azote and hydrogen, what must happen if that mixture be put together with a solution of the yellow prussiate of potash? Supposing 1 equiv. of the said peroxide and 1 equiv. of nitric acid in the acid mixture to act upon 2 equiv. of the yellow cyanuret, we must obtain from such a reaction 1 equiv. of nitrate of potash, 1 equiv. of the red sesqui-ferrocyanuret of potassium, 1 equiv. of deutoxide of azote, and 2 equiv. of water, for

$$(NO_4 + HO_2) + (NO_2 + HO_2) + 2\,(2P\,Cy + Fe\,Cy) = PO\,NO_5 + (3P\,Cy + Fe_2Cy_3) + NO_2 + 2HO.$$

If a glass tube, open at one end, be half-filled with our acid mixture and half with a dilute solution of the yellow prussiate, on mixing the liquids together a lively disengagement of gas takes place; and if the open end of the tube be put into a vessel holding water, a colourless gas will fill the upper part of the tube. On adding oxygen or atmospheric air to the gas disengaged under the circumstances mentioned, the latter will turn brownish red and exhibit all the properties of deutoxide of azote. As soon as the acid mixture comes in contact with the nearly colourless solution of the common prussiate of potash, the latter turns deeply yellow, and it is very easy to ascertain that the coloured fluid contains nitrate of potash, sesqui-ferrocyanuret of potassium, and no trace of the yellow prussiate, provided a sufficient quantity of the acid mixture had been employed. The reactions indicated are therefore such as they ought to be, if, according to our supposition, the acid mixture contains nitric acid and peroxide of azote and hydrogen. I need hardly say that the disengagement of deutoxide of azote and the transformation of the yellow cyanuret into the red one, which take place under the circumstances mentioned, cannot originate in the nitric acid being contained in the acid mixture, for it is well known that dilute pure nitric

acid does not give rise to the reactions described. The cause of those effects must therefore be sought in another substance, and both hyponitric and nitrous acid not being able to coexist with free water, we are not allowed to consider either the one or the other of those acids as that cause. As I have already remarked, the reactions in question can, according to my opinion, only be accounted for in a satisfactory manner by admitting the presence of $NO_2 + HO_2$ in the acid mixture so often mentioned. My experiments have further shown that iodide of potassium, be it solid or dissolved in water, is readily decomposed by ozone, iodine being eliminated. In putting our acid mixture to a solution of the salt mentioned, deutoxide of azote is abundantly disengaged, iodine precipitated, and nitrate of potash formed. As pure nitric acid containing as much water as the said acid mixture, does not act upon the solution of iodide of potassium, it cannot be the nitric acid of our mixture that causes those phænomena, nor can they, from reasons already stated, proceed from hyponitric or nitrous acids.

If we admit that there is, besides nitric acid, some $NO_2 + HO_2$ present in the acid mixture, I think we may easily account for those reactions. $HO_2$ oxidizes the potassium of the iodide, nitric acid unites with the base thus formed, and $NO_2$ is set free.

$$(NO_4 + HO_2) + (NO_2 + HO_2) + PI = PO\,NO_5\,(PO_2\,NO_4) + I + NO_2 + HO.$$

The facts I am about to state are most likely also connected with the subject under discussion.

Largely diluted pure nitric acid, not colouring in the least paste of starch containing chemically pure iodide of potassium, when put for a short time in contact with a number of metals, as zinc, iron, lead, copper, mercury, silver, &c., acquires the property—1. To colour deeply blue the paste mentioned. 2. To transform the yellow cyanuret into the red one. 3. To colour blue the resin of guaiacum. 4. To decompose sulphuretted hydrogen, &c.

Tin is an exception to the rule, for however long dilute nitric acid may have been in contact with that metal, it does not cause the reactions indicated. On the contrary, an acid having the properties mentioned, loses them when mixed in proper quantities with dilute nitric acid which has been in contact with tin. The latter acid has also the power of discharging the colour of paste of starch rendered blue by iodine. From the facts stated, it seems to follow, that on dilute nitric acid being acted upon by oxidable metals, the same oxidizing

agent is produced that forms on mixing hyponitric acid with water; and it appears also that tin engenders with dilute nitric acid a deoxidizing matter, *i. e.* a nitrate of protoxide of tin.

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## CL. *On the Composition of the Fire-Damp of the Newcastle Coal Mines.* *By* Thomas Graham, *Esq., F.R.S.*

SOME years ago I examined the gas of these mines, with the same result as Dr. Henry, Davy and Dr. Turner had previously obtained, namely, that it contains no other combustible ingredient than light carburetted hydrogen. But the analysis of the gas of the coal mines in Germany, subsequently published, showing the presence of other gases, particularly of olefiant gas, has rendered a new examination of the gas of the English mines desirable. The gases were,—1, from a seam named the Five-Quarter seam, in the Gateshead colliery, where the gas is collected as it issues, and used for lighting the mine; 2, the gas of Hebburn colliery, which issues from a bore let down into the Bensham seam—a seam of coal which is highly charged with gas, and has been the cause of many accidents; and 3, gas from Killingworth colliery, in the neighbourhood of Jarrow, where the last great explosion occurred. This last gas issues from a fissure in a stratum of sandstone, and has been kept uninterruptedly burning, as the means of lighting the horse-road in the mine, for upwards of ten years, without any sensible diminution in its quantity. The gases were collected personally by my friend Mr. J. Hutchinson, with every requisite precaution to ensure their purity, and prevent admixture of atmospheric air.

The usual eudiometrical process of firing the gases with oxygen was sufficient to prove that they all consisted of light carburetted hydrogen, with the exception of a few per cent. The results were as follows:—

*Gateshead Gas.*—Specific gravity 0·5802.

| | |
|---|---|
| Carburetted hydrogen . . . . . | 94·2 |
| Nitrogen . . . . . | 4·5 |
| Oxygen . . . . . | 1·3 |
| | 100·0 |

The density of such a mixture is, by calculation, 0·5813.

*Killingworth Gas.*—Specific gravity 0·6306.

| | |
|---|---|
| Carburetted hydrogen . . . . . | 82·5 |
| Nitrogen . . . . . | 16·5 |
| Oxygen . . . . . | 1·0 |
| | 100·0 |

The theoretical density of this gas, deduced from its composition, is 0·6308.

The Hebburn gas was of specific gravity 0·6327.

Seventy-nine measures of the Killingworth gas, mixed with an equal volume of chlorine, left in the dark for eighteen hours, and afterwards washed with alkali, were reduced to 75 measures; from which the presence of 4 measures of olefiant gas might be inferred. But in a comparative experiment made at the same time on 25·3 measures of pure gas of the acetates, mixed with an equal volume of chlorine, a contraction occurred of 1·3 measure; that is in exactly the same proportion as with the fire-damp.

It was observed that phosphorus remains strongly luminous in these gases, mixed with a little air, while the addition to them of one-four-hundredth part of olefiant gas, or even a smaller proportion of the volatile hydrocarbon vapours, destroyed this property. Olefiant gas itself, and all the allied hydrocarbons, were thus excluded.

Another property of pure light carburetted hydrogen, observed by myself, enabled me to exclude other combustible gases, namely, that the former gas is capable of entirely resisting the oxidating action of platinum black, and yet permits other gases to be oxidated which are mixed with it even in the smallest proportion, such as carbonic oxide and hydrogen, the first slowly and the last very rapidly; air or oxygen gas being, of course, also present in the mixture. Now platinum black had not the smallest action on a mixture of the gas from the mines with air. No moisture appeared or sensible contraction, and no trace of carbonic acid could be discovered after a protracted contact of twenty-four hours; while, with the addition of one per cent. of hydrogen, the first effects were conspicuously evident in three minutes, and with the same proportion of carbonic oxide, the gas became capable of affecting lime-water in half an hour. These experiments were repeated upon each of the three specimens of fire-damp.

Potassium fused in the fire-damp did not become covered with the green fusible compound of carbonic oxide, nor occasion any contraction. Indeed, however carefully the heat was applied to the potassium by means of an oil-bath, a slight permanent expansion always ensued. The same thing occurred in pure gas of the acetates. It appeared that potassium could not be heated above 300° Fahr. in pure carburetted hydrogen, without causing a decomposition and the evolution of free hydrogen gas.

The gas was also inodorous, and clearly contained no appreciable quantity of any other combustible gas than light

carburetted hydrogen. The only additional matters present were nitrogen and oxygen; the specimen collected in the most favourable circumstances for the exclusion of atmospheric air, namely, that from the Bensham seam, still containing 0·6 per cent. of oxygen. The gases also contained no carbonic acid.

It is worthy of observation, that nothing oxidable at the temperature of the air is found in a volatile state associated with the perfect coal of the Newcastle beds. The remarkable absence of oxidability in light carburetted hydrogen appears to have preserved that alone of all the combustible gases originally evolved in the formation of coal, and which are still found accompanying the imperfect lignite coal of Germany, of which the gas has been examined. This fact is of geological interest, as it proves that an almost indefinitely protracted oxidating action of the air must be taken into account in the formation of coal; air finding a gradual access through the thickest beds of superimposed strata, whether these strata be in a dry state or humid.

In regard to measures for preventing the explosion of the gas in coal mines, and of mitigating the effects of such accidents, I confine myself to two suggestions. The first has reference to the length of time which the fire-damp, from its lightness, continues near the roof, without mixing uniformly with the air circulating through the workings. It was found that a glass jar, of six inches in length and one inch in diameter, filled with fire-damp, and left open with its mouth downwards, continued to retain an explosive mixture for twenty minutes. Now it is very desirable that the fire-damp should be mingled as soon as possible with the whole circulating stream of air, as beyond a certain degree of dilution it ceases to be explosive. Mr. Buddle has stated, "that immediately to the leeward of a blower, though for a considerable way the current may be highly explosive, it often happens that after it has travelled a greater distance in the air-course, it becomes perfectly blended and mixed with the air, so that we can go into it with candles; hence, before we had the use of the Davy lamp, we intentionally made 'long runs,' for the purpose of mixing the air." It is recommended that means be taken to promote an early intermixture of the fire-damp and air; the smallest force is sufficient for this purpose; as a downward velocity of a few inches in the second will bring the light gas from the roof to the floor. The circulating stream might be agitated most easily by a light portable wheel, with vanes, turned by a boy, and so placed as to impel the air in the direction of the ventilation, and not to impede the draft. The gas at the roof undoubtedly often acts as an explosive train,

conveying the combustion to a great distance through the mine, while its continuity would be broken by such mixing, and an explosion, when it occurred, be confined within narrower limits.

Secondly, no effective means exist for succouring the miners after the occurrence of an explosion, although a large proportion of the deaths is not occasioned by fire, or injuries from the force of the explosion, but from suffocation by the after-damp, or carbonic acid gas, which diffuses itself afterwards through all parts of the mine. It is suggested that a cast-iron pipe, from eight to twelve inches in diameter, be permanently fixed in every shaft, with blowing apparatus, above, by which air could be thrown down, and the shaft itself immediately ventilated after the occurrence of an explosion. It is also desirable that, by means of fixed or flexible tubes, this auxiliary circulation should be further extended, and carried as far as practicable into the workings.

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Nov. 17, 1845.—John Thomas Cooper, Esq., Vice-President, in the Chair.

"Taylor's Calendar of the Meetings of the Scientific Societies of London for 1845 and 1846," presented by the editor.

W. H. Balmain, Esq. was elected a Member of the Society.

The following paper was read:—

## CLI. *Observations on the Resin of the* Xanthorœa hastilis, *or Yellow Gum-resin of New Holland. By* John Stenhouse, *Esq., Ph.D.*

THIS remarkable resin, which is known in commerce as the yellow gum or acaroid resin of Botany Bay, exudes from the *Xanthorœa hastilis*, a tree which grows abundantly in New Holland, especially in the neighbourhood of Sidney. This resin was first described in Governor Phillips's Voyage to New South Wales in 1788. Mr. Phillips states that it was employed by the natives and first settlers as a medicine in cases of diarrhœa. The resin as it occurs in commerce sometimes forms masses of considerable size, but as it is very brittle, although tolerably hard, it usually arrives in the state of a coarse powder. Its colour is a deep yellow, with a slightly reddish shade, considerably resembling gamboge, but darker and less pleasing. The colour of its powder is greenish yellow. When chewed it does not dissolve or stick to the teeth, but tastes slightly astringent and aromatic like storax or benzoin. Its smell is very agreeable and balsamic. When gently heated it melts, and when strongly heated it burns with a strong smoky flame, and emits a fragrant odour

resembling balsam of Tolu. The resin contains a trace of an essential oil, to which much of its agreeable smell is probably owing. This oil passes into the receiver when the resin is distilled with a mixture of carbonate of soda and water, but its quantity is so small that I was unable to examine it more closely. The resin is insoluble in water, but dissolves readily both in alcohol and in æther, especially in the former. Its solution in alcohol has a brownish yellow colour; the addition of water precipitates it as a dark yellow mass, but it does not crystallize out of its alcoholic solution when left to spontaneous evaporation, but remains as a varnish. When digested with strong alkaline lyes, it readily dissolves and forms a brownish red solution; and when the alkali is neutralized with muriatic acid, the resin is precipitated considerably altered as a dark brownish brittle mass. On concentrating the solution out of which the resin has been precipitated, and allowing it to cool, a quantity of impure reddish crystals resembling benzoic acid are gradually deposited. It requires repeated and long-continued digestions with the strongest alkaline lyes to remove the whole of this crystalline acid from the resin, which retains it with very great tenacity. The quantity of the acid is by no means great. It is not easily purified, as its crystals are apt to retain a trace of a reddish colouring matter, from which it is very difficult to free them. The easiest way of getting rid of it, is by dissolving the impure crystals in a small quantity of alcohol and then adding water; the greater portion of the colouring matter is retained in solution, while the crystals are precipitated tolerably white. When purified by repeated crystallizations, they become quite colourless. In appearance, taste, and smell they closely resemble benzoic acid. When dried at 212° F. and subjected to analysis,—

I. 0·2284 grm. of substance gave 0·6005 $CO_2$ and 0·113 HO.

II. 0·2955 grm. of substance prepared on a different occasion gave 0·790 $CO_2$ and 0·1505 HO.

| | Found. | | | |
|---|---|---|---|---|
| | I. | II. | Cinnamic acid. | Benzoic acid. |
| C . | 71·74 | 72·91 | 73·35 | 68·85 |
| H . | 5·49 | 5·65 | 5·32 | 4·91 |
| O . | 22·77 | 21·44 | 21·33 | 26·24 |
| | 100·00 | 100·00 | 100·00 | 100·00 |

It is evident from these analyses that the crystalline acid contains nearly the same amount of carbon and hydrogen as cinnamic acid, with some deficiency however in the carbon. I was led therefore to suspect that it consisted essentially of cinnamic

acid, with probably a small admixture of benzoic acid, a suspicion which subsequent experiments tended fully to confirm; for on heating a quantity of the crystals with some peroxide of manganese and sulphuric acid, oil of bitter almonds was immediately evolved, and on boiling a second portion with hypochlorite of lime, the very peculiar chlorinated oil described in a former paper was also abundantly produced, thus clearly indicating the presence of cinnamic acid. A third portion of the crystals was dissolved in alcohol and left to spontaneous evaporation; it yielded after some time the fine rhombic prisms so characteristic of cinnamic acid when it is crystallized out of alcohol, mixed however with some long acicular crystals, having all the appearance of benzoic acid. I think myself warranted to conclude therefore that Botany Bay resin contains cinnamic acid mixed with a very little benzoic, in which respect it resembles balsam of Tolu, which contains both cinnamic and benzoic acids, though fortunately in much greater abundance.

*Action of Nitric Acid on the Resin.*

When the resin is treated with moderately strong nitric acid in the cold, a violent action ensues with the evolution of nitrous fumes. The resin is completely dissolved if the quantity of the nitric acid is considerable. The colour of the solution is dark red, but by boiling it becomes of a bright yellow colour. The liquid should be evaporated to dryness on the water-bath, to get rid of the great excess of nitric acid. The residue forms a mass of fine yellow crystals, consisting chiefly of carbazotic acid, but mixed with some oxalic and a little nitrobenzoic acids. The nitrobenzoic acid is evidently derived from the cinnamic acid in the resin. The carbazotic acid is easily separated from these other acids by converting it into carbazotate of potash, which is easily purified by one or two crystallizations, and then by decomposing the salt with muriatic acid, pure carbazotic acid may be obtained.

0·3823 grm. of the acid, dried at 212° F., gave 0·442 $CO_2$ and 0·049 HO.

| | Found. | Calculated numbers. |
|---|---|---|
| Carbon . . | 31·53 | 31·37 |
| Hydrogen . | 1·42 | 1·30 |
| Oxygen . . | 67·05 | 67·33 |
| | 100·00 | 100·00 |

0·3975 grm. of the potash salt, decomposed by sulphuric acid and then ignited with carbonate of ammonia, left 0·1300 of sulphate of potash = 17·68 per cent. of potash; calculated quantity 17·60.

The silver salt was also formed by boiling the acid with carbonate of silver. It is a very soluble salt, which crystallizes in fine red-coloured needles. 0·8975 grm. of the salt gave 0·372 Cl Ag=31·22 Ag, or 33·53 per cent. oxide. The calculated numbers are 31·27 per cent. of silver = 33·59 oxide.

The quantity of carbazotic acid which Botany Bay resin yields when treated with nitric acid is so great, and it is so easily purified, that this resin seems likely to prove the best source of that substance. When the resin is subjected to destructive distillation in an iron or copper retort, it yields a very large quantity of a heavy acid oil mixed with a very small quantity of a neutral oil, which is lighter than water. If however the resin has been previously digested with alkaline lyes, so as to remove all the cinnamic and benzoic acids it contains, the heavy oil is obtained as before, but none of the light essential oil. The acid oil is readily soluble in potash and soda lyes; in its smell and properties it resembles creosote; when it is digested with nitric acid, it is wholly converted into carbazotic acid, and when a slip of fir-wood is dipt in it, and then moistened with either muriatic or nitric acid, the deep blue colour passing quickly into brown, so characteristic of hydrate of phenyle, is immediately produced, with which substance the oil appears completely identical. The light oil above mentioned, the quantity of which is extremely small, is separated from the hydrate of phenyle by saturating it with an alkali and distilling the mixture in a glass retort with a gentle heat. In smell and properties it resembles benzin, and is most probably a mixture of benzin and cinnamene; unfortunately the quantity obtained was so small, that I was unable to subject it to more particular examination.

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December 1, 1845.—The President in the Chair.

William Johnson, Esq. was elected a Member of the Society.

The following communications were read:—

CLII. *An Account of various Substances found in the Guano Deposits and in their Vicinity.* *By* E. F. Teschemacher, *Esq.*

REPORTS having been circulated that large quantities of saltpetre (nitrate of potash and nitrate of soda) were to be found of a very good quality in the neighbourhood of the guano deposits on the coast of Africa, numerous vessels were dispatched both from London and Liverpool in search of those valuable substances, particularly as it was considered they might be obtained upon the same terms as Ichaboe guano, namely, for nothing but the labour and expense of fetching

No favourable accounts however have as yet been received as to the success of these undertakings. The evidence of such deposits existing there at all was very unsatisfactory; the circumstance much relied upon was the existence of large beds of nitrate of soda in the neighbourhood of the coast of South America, and large deposits of guano similar in many respects to the deposits of guano on the African coast: there was certainly an abundance of animal matter and ammoniacal salts to furnish the nitric acid, and a temperature high enough to effect the decomposition, but the source from whence the alkaline bases of potash and soda were to be derived was not very evident. The principal source of saltpetre in the East Indies is from numerous districts of nitrous earth found on the surface of the soil, which being compounds of lime and magnesia with nitric acid, they are dissolved out, and the saltpetre subsequently formed by the decomposition of these nitrous compounds by potash salts. The nitrate of soda saltpetre beds in the Province of Tarapaca near Iquiqua on the coast of South America, are the only instances known of the occurrence of saltpetre ready-formed in extensive beds, but even this deposit contains the salt in a state of great impurity.

These explorations, however, on the African coast have brought to light various other substances which have been found there, the details of which are more particularly the object of this communication.

The substances which I shall now describe are found in the guano beds, or in their vicinity, either in a crystalline state, or in distinct masses. The first substance is a crystalline salt, perfectly transparent, with a cleavage and brilliant faces in one direction only; it gives a yellow precipitate with nitrate of silver; gives off ammonia upon application of caustic potash, and when heated to redness loses about 50 per cent. of water and ammonia; I consider it therefore to be *phosphate of ammonia*. The portion of salt I examined consisted only of a few grains, and was consequently too small a quantity to analyse with exactness.

The next substance was also a crystalline salt a little mixed with guano in its cavities; it possessed a cleavage with brilliant planes in two directions: upon examination with the reflecting goniometer, it gave 112° as the measurement of the angle formed by the meeting of the adjacent planes. Upon analysis I found it to consist of—

| | | |
|---|---|---|
| 21·0 | parts of | Ammonia. |
| 55·50 | ... | Carbonic acid. |
| 23·50 | ... | Water. |
| 100·00 | | |

being nearly equivalent to 1 atom of ammonia, 2 atoms of carbonic acid, and 2 atoms of water.

Formula $NH_3 + 2CO_2 + 2HO$,

and is consequently a *bicarbonate of ammonia*.

The third substance was found at Saldanha Bay on the coast of Africa, imbedded in patches in the mass of guano. It is found in distinct crystals with numerous modifications, many of the planes possessing sufficient brilliancy to enable me to measure the angles by the reflecting goniometer. I have given the measurements of one crystal, from which it appears the primary form is the right rhombic prism of 57° 30′ and 122° 30′: it has a cleavage parallel to plane M*. Upon analysis I find this substance to be composed of—

| | | |
|---|---|---|
| 14·30 | parts of | Ammonia. |
| 17·00 | ... | Magnesia. |
| 30·40 | ... | Phosphoric acid. |
| 38·10 | ... | Water. |
| 99·80 | | |

which is nearly equivalent to 1 atom ammonia, 1 atom magnesia, 1 atom phosphoric acid, 5 atoms water.

Formula $NH_3$, MgO, $PO_5 + 5HO$.

It is therefore the *ammonio-magnesian phosphate*. The specific gravity is 1·65, hardness 2; it falls to powder before the blowpipe, giving off water and ammonia. It occurs white, translucent, sometimes coloured brown by the guano; it readily dissolves in weak acids.

This substance is clearly derived from the guano; but being insoluble in water, it must have been held in solution by some of the organic acids of the guano, and deposited therefrom in large crystals, as they are found, but disseminated in patches only of the guano, in various parts of the beds.

This substance not having been found before in a native state, but hitherto only been known as one of the artificial products of the laboratory, must be considered as a new mineral body; I therefore propose to give it the mineralogical name of *Guanite*, this name being derived from the circumstances and locality of its formation.

The source from which the first two substances, namely, the phosphate of ammonia and the bicarbonate of ammonia, are derived, is clearly the percolation of water through the guano beds dissolving out these salts, which running into lower

* See the angular measurements subjoined.

situations may be detained in lagoons and hollows of rocks, where being subject to the high temperature of the climate they would be evaporated down, leaving these salts in the crystalline state described. As guano contains abundance of these two salts, it is possible there may exist considerable masses of them; should this be the case, it is evident that to the chemist in particular it would be of great interest as an additional source of these valuable salts.

The chance of finding any considerable quantity of guanite in the state of crystals is not great, but as it forms one of the ingredients of guano it is a substance of some importance. The application of it as a manure in combination with other ingredients is likely to be highly beneficial, it being a compound containing two important substances in an insoluble state, namely, ammonia and phosphoric acid; these may be taken up by plants only as they may be required, and not be liable to be dissolved out of the soil or evaporated like other ammoniacal salts.

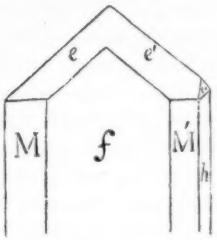
The last substance which I shall describe was also found imbedded in the guano from Saldanha Bay; it consists of small globular particles composed of concentric laminæ slightly adhering together, of a yellowish white colour, containing in places portions of a similar nature, which on fracture have appearances of an organic structure like bone, but on examination by the microscope proved to be portions of shells resembling Nummulites. On analysis I found the substance to be composed of—

| | | |
|---|---|---|
| 37·50 | parts | Carbonate of lime. |
| 32·50 | ... | Carbonate of magnesia. |
| 12·00 | ... | Phosphate of lime. |
| 12·00 | ... | Water with a little ammonia and animal matter. |
| 3·00 | ... | Sand. |
| 2·50 | ... | Alkaline sulphates and chlorides. |
| 99·50 | | |

There does not appear to be any great quantity of this substance. How it has been formed it is difficult to imagine; the composition is so very different either from that of bones or shells, particularly in regard to the large quantity of carbonate of magnesia which it contains. It is however probable that both bones and shells form the base of this substance, and that partial decomposition having taken place, the magnesia may have subsequently entered into combination with the carbonate and phosphate of lime.

*Measurements of Guanite.*

| | | | |
|---|---|---|---|
| M on M′ . | 57°·30 | M′ on *e′* . | 142°·10 |
| M on *f* . | 118°·30 | *h* on *c* . . | 133°·20 |
| M′ on *f* . | 118°·30 | *e* on *e′* . . | 91°·50 |
| M′ on *h* . | 151°·00 | *e* on *f* . . | 112°·20 |
| *f* on *h* . . | 89°·30 | *e′* on *f′* . | 112°·20 |
| M on *e* . | 142°·10 | *e* on *c* . . | 142°·10 |




## CLIII. *On some Chemical Effects produced by Platinum.* By *Dr.* C. F. Schœnbein.

SOME time ago I published an account of a series of experiments made with the resin of guaiacum, from which it appeared that the substance named is instantly rendered blue, not only by chlorine and nitrous acid, but also by bromine, iodine, ozone, and a number of metallic peroxides.

Free oxygen, be it pure or mixed with nitrogen, hydrogen, and carbonic acid gas, does not act in the dark upon that resinous matter, and comparatively very little when exposed to the action of solar light. From these facts, it becomes manifest that oxygen must have assumed a peculiar condition of chemical excitement before it is capable of causing the reaction mentioned. The beautiful experiments both of Davy and Dœbereiner have demonstrated that platinum has the power to occasion the oxidation of a number of substances under circumstances in which that chemical action would not take place without the agency of that metal. The blue coloration which the resin of guaiacum assumes under certain circumstances is most likely dependent upon a partial oxidation of that substance, and the latter being so very sensible to oxygen, that happens to be chemically excited, it could easily be conjectured that platinum in a state of minute mechanical division put in contact with the resinous substance mentioned, might cause the oxidation of the latter in the same manner as that metal occasions the oxidation of hydrogen, æther and alcohol. The facts I am going to state will show that the correctness of this conjecture is fully borne out by experiment.

Newly-prepared spongy platinum being placed upon a piece of filtering paper that had previously been drenched with an alcoholic solution of resin of guaiacum, caused rather rapidly the appearance of blue spots at the place where the metal had been in contact with the resinous solution. My experiments

have further shown that that reaction takes place the more rapidly and intensely the more divided the platinum happens to be of which we make use in the experiment described. What is called Platinum Black acts therefore more energetically than spongy platinum does. From the facts stated, it appears that platinum in a state of minute mechanical division conducts itself towards resin of guaiacum like the simple halogenous bodies, ozone and a number of metallic peroxides. These facts demonstrate also that the coloration of the resinous matter being caused by platinum, belongs to that series of phænomena which takes place when that metal is put in contact with a mixture of oxygen and hydrogen, oxygen and vapour of æther, &c.

In the paper above alluded to, I have pointed out the remarkable coincidence that all the substances having the power of rendering blue the resin of guaiacum possess also the property of decomposing iodide of potassium, transforming the yellow prussiate of potash into the red one, and I add, decomposing sulphuretted and iodurettted hydrogen, transforming sulphurous acid into sulphuric acid, and destroying organic colouring matters. We shall presently see that platinum in a state of minute mechanical division has the same power.

If a crystal of pure iodide of potassium be put upon a piece of filtering paper that has previously been moistened with distilled water and spongy platinum be placed upon that paper, the spot touched by the metal assumes rather rapidly a brownish red colour. This coloration does not result from free iodine, but is most likely due to a compound consisting of periodide of platinum and iodide of potassium. That conjecture is founded upon the following facts. If a solution of iodide of potassium is put in contact with spongy platinum, or platinum black, the former assumes a perceptibly red colour, which disappears on heating the solution to its boiling-point. Now it is well known that the compound before mentioned yields with water a red solution, the colour of which is destroyed by heat. Neither the red solution nor the brownish-red spots before mentioned are able to render blue paste of starch, another proof that there is no free iodine in the case. The reaction described is most likely brought about in the following manner: the chemically excited oxygen surrounding the spongy platinum decomposes iodide of potassium, a peculiar peroxide of potassium being formed and iodine eliminated. The latter in its nascent state combines with platinum to produce the periodide of that metal, which itself unites with iodide of potassium into that compound, yielding with water a red solu-

tion. It is worthy of remark, that a solution of iodide of potassium having been treated with spongy platinum, enjoys the property of colouring blue the paste of starch on being mixed with dilute and pure sulphuric acid. The same reaction is exhibited by the same solution after it has been treated either with ozone or peroxide of lead. If some drops of a weak, *i. e.* colourless solution of the yellow prussiate of potash, be added to platinum black, that solution assumes a perceptibly yellow colour, and yields with a solution of chemically pure sulphate of protoxide of iron a blue precipitate.

From these facts, it seems to follow that platinum has the power to transform the yellow prussiate into the red one. Some years ago I tried to show that spongy platinum being placed in an atmosphere of sulphuretted hydrogen, loses its property of acting upon detonating gas, on account of a film of sulphur being deposited on the surface of the metal. Such being the case, it would follow that spongy platinum has the property to decompose sulphuretted hydrogen.

Colourless hydriodic acid, on being mixed up with some platinum black, assumes a brownish yellow colour, which reaction indicates an elimination of iodine.

Several chemists, particularly Dœbereiner, Phillips, and Brunner, have ascertained that spongy platinum produces sulphuric acid on being placed in contact with moist oxygen and sulphurous acid, and there is no doubt that platinum black put into sulphurous acid gives rise to the formation of sulphuric acid. Moist filtering-paper being coloured by a solution of indigo and put in contact with spongy platinum for about twenty-four hours, appears entirely bleached at those spots which had touched the metal. I have repeated this experiment more than thirty times, and always with the same result. This remarkable fact proves that platinum in a state of minute mechanical division, has the power of destroying organic colouring matters, and acts as a real bleaching agent. Before passing to other subjects, I must not omit to mention a circumstance which seems to me meriting some attention. It is a curious fact, which has not escaped the notice of chemists, that in more than one case platinum acts exactly like common electricity, both of them determining at the common temperature, for instance, the oxidation of free hydrogen. Now it being well known that nitric acid is formed if electrical sparks are made to pass through moist air, it seemed to me within the reach of possibility, that the same acid might be produced by platinum, if that metal in a state of minute mechanical division were placed in contact with moist atmospheric air. With the view of ascertaining the

correctness of that conjecture, I put a piece of moist litmus paper in close contact either with spongy platinum, or with platinum black. In some cases part of the paper exhibited a slight reddish coloration, part of it proved to be entirely bleached, or nearly so. I must, however, not omit to state, that in the great majority of my experiments I obtained bleaching effects only, and no reddening of the litmus paper whatever. I am unable to account for the difference of the results mentioned. Was the reddening of the litmus paper caused by some traces of nitric acid formed under the circumstances indicated? I am not prepared at all to answer that question. If nitric acid should however happen to be produced under the circumstances mentioned, it would be a fact, in my opinion, not very difficult to be accounted for. In whatever state the oxygen surrounding platinum may be, certain it is that that state is such as to render oxygen very apt to combine at the common temperature with a number of oxidable substances that would not be oxidized by common oxygen without the presence of platinum. The formation of nitric acid taking place under the circumstances mentioned, would indeed be a fact very similar to the combustion of detonating gas caused by platinum. I repeat, however, that I consider the generation of nitric acid brought about by the agency of platinum, as far from being established by decisive facts.

The voltaic character of bodies being so intimately connected with their chemical nature, that in most if not in all cases we may infer the one from the other, the fact I am going to state merits our attention. Chlorine, bromine, iodine, ozone, and a number of metallic peroxides, enjoy considerable electro-motive powers, which are of such a kind as to render those bodies what is commonly called electro-negative. Hence it comes that a piece of metal being covered with any one of the bodies named, bears to another common piece of the same metal the same voltaic relation as copper does to zinc. According to the experiments of De la Rive and some other philosophers, platinum foil being covered with some spongy platinum, is negative to common platinum plate, a fact which proves that in a voltaic point of view there exists a great analogy between the simple halogenous bodies, ozone and metallic peroxides on one side, and spongy platinum on the other.

After having stated a number of facts which demonstrate the highly oxidizing powers of platinum, we ask in what manner does that metal exalt the chemical activity of oxygen? This question has occupied many philosophers, and been answered in very different ways. Faraday and Dœbereiner

ascribe to platinum the power of condensing oxygen so much as to deprive that element of its gaseous condition, and think that condensed state to be the true cause of the oxidizing powers of platinum. Others (De la Rive and Gmelin) presume that oxygen is capable of chemically uniting with that metal, and with those philosophers it is the oxide of platinum that occasions the oxidation of hydrogen, &c. Berzelius holds the opinion that the oxidations caused by platinum are catalytical phænomena, *i. e.* effects produced by some unknown force being innate to that metal and exalting the chemical attractive powers of oxygen.

It is not my intention to enter into a discussion of those opinions; I shall confine myself to a few general remarks upon that interesting subject. As the common oxides of platinum are not acted upon (at the common temperature) by free hydrogen, as platinum foil or wire, that causes at a moderate temperature the combustion of detonating gas, exhibits a perfect metallic surface, while the thinnest film of an oxide diminishes or destroys the lustre of any metal, and as platinum is a body that has a very weak affinity for oxygen, I think that that metal is not capable of combining directly with the oxygen of the air, and that De la Rive's view of the subject is erroneous. But how is it with Faraday's and Dœbereiner's theory of the matter in question? It seems indeed to be the true one. Satisfactory however as that hypothesis may appear, it is nevertheless possible that the oxidizing action of platinum may depend upon a cause different from what the philosophers mentioned consider as such.

We know that phosphorus being put in contact with moist atmospheric air gives rise to the formation of a highly oxidizing agent, which, as it has been shown elsewhere, seems to be a peculiar compound of water and oxygen, and enjoys the power of oxidizing a great number of substances at the common temperature. Now if phosphorus enjoys that property, it seems possible that some other substances, for instance platinum and iridium, may do the same. In other terms, it appears possible that platinum has the power to engender out of free oxygen and water a highly oxidizing peroxide, which surrounding that metal empowers the latter to cause all the oxidations above mentioned. In comparing the chemical properties of platinum, when minutely divided, with those of ozone, we cannot help being struck by their great similarity, as will appear from the following statements:—

1. Both substances possess a negative electro-motive power.
2. Both of them destroy organic colouring matters.
3. Both of them render the resin of guaiacum blue.

4. Both of them decompose iodide of potassium.

5. Both of them change the yellow prussiate of potash into the red one.

6. Both of them transform sulphurous acid into sulphuric acid.

7. Both of them decompose oxalic and formic acids.

8. Both of them act in a similar way upon æther and alcohol.

Great as the similarity of properties may be, it does not follow that platinum owes its oxidizing powers to a film of peroxide of hydrogen being formed round the metal by a catalytical action of the latter. I have not yet succeeded in producing, by the means of spongy platinum and moist air, an atmosphere exhibiting the peculiar electrical smell, bleaching power and oxidizing properties which belong to ozone. Considering the great volatility of the last-named substance, we should suppose that it ought to disperse into the surrounding medium as soon as formed; or should ozone be retained by platinum in a way similar to that in which we think oxygen is attached to and condensed around that metal? Supposing oxygen to be an odoriferous substance, it is manifest that the oxygen actually condensed by platinum, could not affect the olfactory nerves.

Another objection might be raised to the conjecture, that it is a film of peroxide of hydrogen, to which platinum owes its oxidizing powers, from the fact that Thenard's oxygenized water is really decomposed by platinum. Considering however that ozone is in some respects strikingly different from Thenard's compound, having for instance a peculiar odour, being insoluble in water, transforming both metallic silver and its basic oxide into a peroxide, it appears possible that ozone is capable of existing in the closest contact with platinum without suffering decomposition. I am not aware of spongy platinum or platinum black having been treated with anhydrous oxygen, and I do not know whether it has been ascertained if the latter is absorbed as easily by that metal as moist oxygen. It is equally unknown to me whether platinum, after being placed in dry oxygen or air, exhibits the same properties as platinum after being exposed for some time to the same gases when moist. If the oxidizing powers of platinum should depend upon a film of peroxide of hydrogen attached to that metal, it is obvious that spongy platinum, freed from its adhering water and placed within completely dry oxygen, could not assume oxidizing properties. Supposing however that spongy platinum acquires oxidizing powers under the circumstances mentioned, we may nevertheless imagine that those powers depend upon a film of per-

oxide of hydrogen surrounding that metal. De la Rive's and Marignac's experiments have shown that oxygen obtained from fused chlorate of potash, on being exposed to the action of electrical sparks, yields perceptible quantities of ozone. Now, taking that odoriferous substance for a peroxide of hydrogen, we must admit that even that oxygen, which is considered as absolutely anhydrous, still contains traces of aqueous vapour. Taking for granted the humidity of what is called dry oxygen, we may easily conceive how platinum brought into an anhydrous mixture of oxygen and hydrogen could cause the combustion of the latter. Out of some oxygen and the traces of water still contained in what is considered anhydrous detonating gas, a film of peroxide of hydrogen would be formed around the spongy platinum; that peroxide, in the very moment of its being engendered, would oxidize a neighbouring portion of free hydrogen. The heat resulting from that oxidation would determine another portion of hydrogen to unite with oxygen. The heat proceeding from that chemical union would occasion the combustion of an additional portion of hydrogen, and so on until the whole of the detonating gas should be consumed. The minute quantity of the peroxide of hydrogen attached to the spongy platinum would act like a small common or electrical spark, which, as we well know, is capable of setting the largest volume of detonating gas on fire. Electrical sparks acting upon a mixture of oxygen and hydrogen, exactly in the same way as spongy platinum does, and it being a well-ascertained fact that ozone makes its appearance on causing common electricity to pass through (moist) oxygen, it is possible that electricity and platinum occasion the oxidation of hydrogen, because both of them are able to produce ozone, and that it is to the agency of that odoriferous substance that we are to ascribe the chemical effect mentioned. That conjecture must become still more plausible, if we take into account the fact that spongy platinum acts in a variety of other cases exactly like ozone. Taking this view of the case, we could not admit that an electrical spark has the power to cause directly the formation of water out of detonating gas, but should be obliged to consider the oxidation as occasioned by the ozone being formed under electrical influence out of aqueous vapour and oxygen. In other terms, we are obliged to ascribe the oxidation to the same cause from which we derive the decomposition of iodide of potassium, the transformation of the yellow prussiate of potash into the red one, the destruction of vegetable colouring matters, the turning blue of the resin of guaiacum, the transformation of the protoxide of lead into the peroxide,

&c., brought about by the electrical brush. Now, as it can hardly be doubted any longer that the chemical effects just stated are due to ozone produced by electricity, the conjecture, according to which free hydrogen may also be oxidized by electrical ozone, seems to be very probable. Indeed, if potassium, the hydrogen of colouring matters, the oxide of lead, &c., are oxidized by the oxygen of electrical ozone, why should free hydrogen make an exception to the rule?

But however that may be, the subject under discussion seems to be interesting, and I add, still obscure enough to offer an inducement to chemists to apply themselves to its elucidation by further investigations. The matter merits our attention the more that it bears so close a relation to that series of chemical phænomena which are called catalytical actions, and which certainly belong to the most enigmatical facts of our science.

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## CLIV. *On the Wax of the Chamærops.* *By* J. E. Teschemacher, *Esq.*

ABOUT three millions of palm leaves are annually imported into the United States of America, for the purpose of being manufactured into hats. They come tied in bundles, called in Spanish *Esteras*, each *estera* weighing from 50 to 60 pounds; these are the palmate part of the leaf with a small portion of the petiole; this last weighs one-eighth of the leaf. The palm from which the leaves are cut in Cuba and other parts of the West Indies for this purpose is a Chamærops, a low-growing species, not differing I believe from the *C. humilis* of the southern sections of the United States, except in being much more robust in habit. The *C. humilis* of the United States is too soft and yielding for this manufacture. I have cultivated the plant from Cuba for five or six years, and was unable to discover any difference in foliage; but I have never seen the fruit of either. The leaf of the Chamærops spreads out nearly horizontal with folds, precisely like those of a lady's fan. On opening these folds, when they arrive in the United States in their dried state, there is a quantity of white flaky powder, under this is the bright varnish which covers the whole surface of the leaf; both these are true vegetable wax. From one of these palm leaves I obtained, by passing the thumb down the folds, 90 grains of the white wax in powdery flakes, and by boiling the leaf, after cutting in pieces, in alcohol, 300 grains more of a grayer coloured wax.

At the manufactory the leaves are often bleached by the

fumes of sulphurous acid gas, and then split by machinery into very thin strips; this division cracks off of course a large portion of the brittle varnish, which, together with the white powder, falls to the ground, is swept together and burnt or thrown away. The weight of this substance destroyed annually probably exceeds one hundred thousand pounds.

On treating this substance with a small quantity of boiling alcohol, it may, like other wax, be separated into cerine and myricine.

The powdery flakes first obtained contain about 80 per cent. myricine and 20 per cent. cerine, but the wax obtained from boiling the leaf in alcohol contains scarcely any myricine. This is easily accounted for; the flakes, being the brittle and more resinous part, break off readily; while the alcohol, which acts on the leaves, dissolves only the cerine, leaving the myricine undissolved; this might no doubt be obtained by increasing the quantity of alcohol and continuing the process, if it were desirable. In bees' wax the proportions of these two substances vary also, the cerine from 70 to 90 per cent., myricine from 10 to 30 per cent.; and it is probable that the more or less brittle quality of all wax depends on the relative quantity of these two ingredients.

The wax of *Ceroxylon audicola*, a very lofty palm, found by Humboldt at Quindin on the Andes, has been analysed, and found very nearly to resemble bees' wax in its ultimate principles.

| | Bees' wax. | Palm wax. |
|---|---|---|
| Carbon . . . . . | 80·14 | 80·28 |
| Hydrogen . . . . | 14·08 | 13·20 |
| Oxygen . . . . . | 5·78 | 6·52 |

To obtain this wax, the outer portion of the trunk is rasped or scraped, the raspings are heated in water, the wax swims at the top, the other parts fall to the bottom, the wax is collected, made into small balls, and dried in the sun; it has a deep yellow colour, and when the resinous part (myricine?) is melted it has the appearance of amber; after the separation of the wax and resin from the produce of Ceroxylon, there remains in the alcohol a bitter yellow substance, supposed to be a vegetable alkaloid. This yellow substance separates also from the wax of the leaf of Chamærops, but I think it is not an ingredient in the wax, but of other parts of the juices dissolved by the alcohol.

The production from the juices of plants by a purely vegetable function of wax scarcely differing from that deposited in their hives by bees is calculated to throw light on the question of the formation of this substance by these insects, and

also merits the careful examination of those who are entering into the study of the various transformations of the vegetable juices at different periods of their progress towards maturity.

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Dec. 15, 1845.—The President in the Chair.

Several of the late Numbers of the Transactions of the Imperial Academy of St. Petersburgh were presented to the Society's Library, by the Academy.

W. A. Miller, M.D., Alfred S. Taylor, Esq., Benjamin Brodie, Esq., and J. M. Neligan, M.D., were elected Members.

The following papers were read:—

## CLV. *New Researches upon Aniline.* *By* A. W. Hofmann, *Ph.D.*

IN my former papers upon aniline I had repeated opportunities of pointing out the remarkable analogy which exists between this body and ammonia, and at the conclusion of my memoir on chloranilin and bromanilin, I announced the existence of a compound, which may be considered as urea, in which ammonia is replaced by aniline.

The discovery of this substance opened a new field for research, inasmuch as it was to be expected that all the relations exhibited by ammonia, and the metamorphoses it undergoes, might be realized with aniline.

A short time after this communication, M. Gerhardt, in proceeding in this direction, has prepared some products belonging to the same series, which are formed when *oxalate of aniline* is subjected to dry distillation, or when *chloride of benzoyl* is acted on by aniline. I also have prepared these bodies, but shall not enter into details upon them in this preliminary note, in which I intend to describe some further results at which I have arrived.

The action of the vapour of cyanic acid upon aniline is rather complicated; *a normal cyanate of aniline* (*urea of aniline*) is best prepared by mixing a solution of sulphate of aniline with cyanate of potassa. The liquid, after the lapse of a few moments, becomes turbid, and in an hour the whole solidifies into a crystalline mass. By a simple recrystallization from water the new compound is obtained in a state of perfect purity.

The combustion of this substance furnished results corresponding to the formula

$$C_{14}\,H_8\,N_2\,O_2 = C_{12}\,H_7\,N,\,HO,\,CyO\,;$$

*i. e.* urea, in which the ammonia is substituted by an equivalent quantity of aniline.

From the properties of this compound, it is evident that the elements of aniline and cyanic acid undergo a similar transposition to that of the same acid and ammonia when forming urea.

The body $C_{14}\,H_8\,N_2\,O_2$

is not the ordinary cyanate of aniline; it crystallizes without change from a concentrated solution in potassa, and acids disengage neither cyanic acid nor carbonic acid.

The comportment of aniline with *cyanic acid* induced me to subject it also to the action of *cyanogen* and *chloride of cyanogen*. In these reactions a series of new crystalline compounds is obtained, which are still under examination.

Not less remarkable is the action of *sulphide of carbon* upon aniline. When left in contact for some time with this compound, aniline with evolution of hydrosulphuric acid is converted into a white crystalline mass, which is difficultly soluble in alcohol, and may be purified with great facility. The analysis of this new compound yielded numbers corresponding with the following formula,

$$C_{13}\,H_6\,N\,S,$$

*i. e.* aniline, which has lost 1 equivalent of hydrogen, and has assumed in its place a compound of carbon and sulphur CS, which corresponds in composition to carbonic oxide.

Aniline . . . . $C_{12}\,H_7\,N$
Sulphocarbanilide . $C_{12}\,H_6\,N$, C S.

This peculiar compound, which is neither acid nor base, is likewise obtained in a most interesting transformation, *i. e.* the decomposition of sulphocyanate of aniline by destructive distillation.

The *sulphocarbanilide*, as we may provisionally term this new compound, is only slowly changed by reagents. The continued action of an alcoholic solution of potassa however decomposes it. After three or four hours' boiling the solution contains a large proportion of sulphide of potassium, and on cooling deposits a substance crystallizing in large brilliant needles, which is a new compound.

By analysis the numbers obtained gave the following formula,

$$C_{13}\,H_6\,NO,$$

which shows that these crystals are formed simply by an exchange of the sulphur of the former compound with the oxygen of the potassa.

Other oxides produce the same effect as potassa. On boiling sulphocarbanilide with oxide of mercury the red colour soon disappears, black sulphide of mercury being formed.

According to the above formula, this new substance, which is also an indifferent body, may be considered as aniline which has lost 1 equivalent of hydrogen and assumed the elements of carbonic oxide.

Aniline . . . . $C_{12} H_7 N$,
Carbanilide . . . $C_{12} H_6 N, C O$;

and this view suggested to me at once another experiment, which was quite successful.

If the above-given formula expresses the true composition of this substance, if it be indeed *carbanilide*, it was extremely probable, if not certain, that it might be produced by the direct action of *chloro-carbonic acid* (*phosgene gas*) upon aniline.

$$\underbrace{C_{12} H_7 N}_{\text{Aniline.}} + \underbrace{CO Cl}_{\text{Phosgene.}} = \underbrace{C_{12} H_6 N C O}_{\text{Carbanilide.}} + HCl$$

On introducing aniline into a balloon filled with *chloro-carbonic acid*, the glass became so hot that it burst. On cooling, the liquid solidified into a white crystalline mass, which by the action of water was resolved into hydrochlorate of aniline and carbanilide.

This is indeed a far easier way of obtaining this substance in the state of purity.

On mixing aniline with *oil of mustard*, at first no change was observed; after the lapse of some months however the solution had deposited splendid four-sided tables, constituting evidently the compound corresponding to thiosinnamine.

When brought in contact with *tritochloride of phosphorus* or *chloride of silicon*, aniline is likewise converted into crystalline compounds.

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## CLVI. *On Electrical Endosmose.* *By* Mr. James Napier.

THAT two dissimilar solutions, separated by a porous partition, will pass the one into the other, is a phænomenon long observed, the only necessary condition being that the liquids have a strong tendency to combine, and that the one is more capable of entering into or wetting the porous partition than the other. The liquids eminently fitted to effect this are alcohol and water, and saturated solutions of some salts and pure water. But the phænomenon of endosmose takes place also when an electric current passes through liquids separated by a porous partition. When all the above conditions are absent, and even when these conditions are present, the endosmotic current will follow the electric, although in a contrary direction to that which would take place were

there no electric current passing, showing that, under these circumstances, it has its origin in the passage of the electric force. This fact was first made known by Mr. Porrett in the Annals of Philosophy for 1816.

The object of this paper is not to define the cause, but to point out the different conditions of electrical endosmose, and the important part it plays in electro-chemical investigation.

The conditions under which electrical endosmose are observed, are, that the two metals constituting a battery, or the two electrodes of a battery, be placed in separate vessels or divisions of the same vessel; one of the vessels, or partition, being composed of a material sufficiently close in texture to prevent the mixture of the two liquids, and porous enough to allow the electricity to permeate through it. The substances generally used are bladder, parchment, unglazed porcelain, &c. The last is what I have generally used in the experiments to be detailed.

The general effects of electrical endosmose are, a portion of the positive solution passes along with the electric current into the negative solution, not by electrolytic action, as has been generally supposed, but by endosmotic action; and this endosmotic current is confined to the direct influence of the electric current, or facing the metals composing the electrodes or battery. There are some circumstances in which the positive solution gains in quantity, making an apparent current contrary to the electrical; these will be referred to as we proceed.

Electrical endosmose manifests itself in two ways, or rather is of two kinds, which may be distinguished as the *measurable* and the *unmeasurable*, the former being the result of the transfer of water from one cell to another, the latter of a salt or acid held in solution, and which is being decomposed; this may take place to an extent equal to the whole salt held in solution in the positive cell without the quantity of the two solutions being materially altered; and that this transfer is from endosmose will be best illustrated by detailing a few experiments, stating however that the investigation necessarily involves a great number of experiments, the whole of which I cannot detail, and the conclusions come to have been the result of these. It may be stated here that the vessel or division in which the positive electrode or metal is placed is termed the positive solution, and the negative division the negative solution.

I. 20 ounces of water, in which were dissolved 500 grains of sulphate of copper, were made the positive solution, and other 20 ounces of water, with 500 grains of sulphate of cop-

per, were made the negative solution. A copper electrode, previously weighed, was put into each of these solutions and connected with a Wollaston's battery of nine pairs, the current allowed to pass until the negative solution was completely exhausted of copper, which required sixty-four hours, the battery not renewed during the experiment. At the end of the experiment, the electrodes being again weighed, the positive had lost 257 grains, the negative had increased 250 grains. The positive solution had lost 6 ounces by measure, the negative had gained 4 ounces. The greatest portion of this change took place within the last ten hours. The 2 ounces lost are mostly from evaporation. The positive solution was evaporated and crystallized, and there were obtained 905 grains of sulphate of copper, 95 less than was originally dissolved; but the partition being saturated with salt may account for a portion of the loss. The 500 grains which were originally in the negative solution would only contain 127 grains of metallic copper; but there is nearly double of this deposited, showing that the salt had been transferred by some means from the positive to the negative, in quantity amounting to nearly the whole of the salt originally dissolved in the positive solution.

II. 100 grains of sulphate of copper were dissolved in 4 ounces of water and put into each division, in the same manner as the last experiment. The partition in this case was much closer in texture than the other; the same battery power was used, and continued till the negative solution was exhausted, which was nineteen hours. The negative electrode being weighed, it had increased 34·4 grains; the negative solution had increased one-fourth of an ounce; the positive solution had lost three-eighths of an ounce. Comparing this experiment with the last, there is a great discrepancy, the only known cause being the closer texture of the diaphragm; the transfer of the salt is only in the proportion of one-third that of the former, and the measurable endosmose is still further out of proportion, being only one-sixteenth; while the amount of decomposition is only one-seventh of the 500 grains. The electrodes in both experiments were the same in size.

The question now suggested itself whether the transfer of the copper salt from the positive to the negative cell was the result of endosmose or of electrolysis, corresponding with the results of the late Professor Daniell and Professor Miller, who supposed that certain bases underwent electrolytic transfer in fractional proportions, and that these proportions might vary according to the texture of the diaphragm, or that kind of peculiar resistance given to the passage of a current when passing from one solution to another.

In order to determine which was the true cause, the negative cell was charged with a weak solution of caustic potash, the positive being sulphate of copper; gas was freely evolved from the negative electrode; in a little time the porous diaphragm facing the electrodes became coated with oxide of copper, which greatly retarded the current, and made it necessary to use a more powerful battery. After twelve hours, the oxide which had accumulated upon the diaphragm and at the bottom of the positive cell was carefully collected, washed, dried, and weighed 7·3 grains. The potash of the positive solution being neutralized by muriatic acid, had a solution of chloride of barium added, which gave a precipitate of sulphate of barytes weighing 26 grains, equal to about 9 grains of sulphuric acid. From this it appeared that the copper had passed from the positive to the negative as sulphate of copper, and therefore not by electrolysis.

In repeating similar experiments with very dilute alkaline and earthy salts in the negative cell, I have observed that the oxide of copper formed being a conductor of electricity, it often floated between the diaphragm and negative electrode as a kind of spongy fibre, and conducted the electricity through it as a solid, constituting its extremity in connexion with the porous partition into the electrode, the result being the reduction of the oxide in and upon the diaphragm, closing it up with metallic copper, similar to that observed in the operations of electro-metallurgy when any of the electrodes are allowed to touch the diaphragm. It has often surprised me how minute a fibre would connect the electrode and cell and produce a wide-spreading result.

A solution of cyanide of potassium was next tried in the negative cell, having sulphate of copper in the positive; the current passed four hours. The cyanide solution smelt strongly of hydrocyanic acid; the solution was found to contain both copper and sulphate of potash; the quantities were not determined.

The next object was to use two salts of such a character that if that from the positive cell passed to the negative by endosmose it would remain in solution; if by electrolysis, the base would be reduced to the state of an insoluble oxide. The negative was accordingly charged with a solution of caustic potash, and the positive with cyanide of copper and potassium, the latter in excess. After eight hours, during which gas was freely evolved from the negative electrode, and upon it was a small portion of copper powder, no oxide was formed; the solution contained cyanide of potassium and copper, the latter being precipitated by hydrochloric acid and fused, gave

3·5 metallic copper, with strong smell of hydrocyanic acid. From this it appeared that both the copper and potassium salt were transferred by endosmose. The double cyanides of potassium and silver and of potassium and gold were next substituted for the copper in the positive cell with similar results. Nitric acid was also substituted for the caustic potash in the negative cell, with the double cyanides of copper, silver and gold in the positive, which would give the contrary result of last experiments, namely, precipitating the metals if transferred by endosmose, but dissolving or holding them in solution if transferred by electrolysis. In a short time, in each experiment, the surface of the porous diaphragm facing the negative electrode became coated with the cyanide of the metal, which accumulated and dropped to the bottom of the vessel. At the termination of the experiments the acid solution smelt strongly of hydrocyanic acid, and contained much nitrate of potash. With the gold and silver salts, the acid solution had not the slightest indication of their presence in solution, but with the copper there was a considerable portion present, which was owing to the cyanide of that metal being decomposed by nitric acid; but this experiment being repeated with the copper cyanide in the positive and sulphuric acid in the negative, no trace of copper in solution was found in the acid.

The next experiment was to determine if any portion of the potassium of the potash salt was transferred by electrolysis; for this purpose two porous vessels were employed, one filled with a solution of cyanide of potassium, the other with dilute nitric acid; these were placed in a glass vessel containing a solution of nitrate of silver; the positive electrode was placed in the cyanide of potassium, the negative in the nitric acid. The cyanide of potassium which passed from the positive cell to the silver solution in the glass vessel was decomposed, producing cyanide of silver and nitrate of potash. After twelve hours, the cyanide of silver formed was carefully collected, washed and dried; it weighed 65·6 grains; the remaining silver solution had as much muriatic acid added as precipitated the silver. The clear filtered solution was now evaporated to dryness and kept for some time at the point of fusion. There were obtained 28 grains of nitrate of potash, which is 4 grains less than the equivalent of cyanide of silver obtained; but the nitric acid in the negative cell also contained a little nitrate of potash and silver, which had passed from the glass vessel, and will account for this loss. From these, and a variety of other experiments of a similar kind with different salts, I consider that no base of an electrolyte is transferred by electrolytic action, but that salts being electrolysed are all

transferred more or less from the positive to the negative electrodes by endosmose, and that the amount of this varies according to the texture of the porous diaphragm, the power of the electric current, and various other modifying circumstances, which will be apparent as we proceed with the inquiry into the cause and circumstances of electrical endosmose.

In referring to the first experiment, it was observed that the greatest amount of measurable endosmose took place during the last ten hours when both solution and battery were nearly exhausted. 500 grains of sulphate of copper were again put into each cell, the solutions accurately measured, and the current of 9 pairs passed for twenty hours. The deposit on the negative electrode was 116·3 grains; this solution had increased in measure three-eighths of an ounce, the positive had lost half an ounce; being evaporated and crystallized, the negative gave 226 grains crystals, the positive gave 749 grains. In this experiment we have 184 grains of the salt transferred, and only three-eighths of an ounce of measurable endosmose.

960 grains of sulphate of copper were dissolved in 20 ounces of water and put into the negative cell, while the positive was charged with dilute muriatic acid. A battery of 12 pairs was connected and kept in action twenty-four hours; it was then found that the negative electrode had increased in weight 178 grains, and the solution had gained in measure $2\frac{1}{2}$ ounces. A small portion had nitrate of silver added, which gave a slight milkiness, but not amounting to a precipitate. The whole solution of the negative cell, being evaporated and crystallized, gave sulphate of copper 463 grains. This shows a transfer of sulphate of copper from the positive solution equal to 162 grains. The positive solution was of a deep blue colour, it had lost by measure $2\frac{1}{4}$ ounces; the electrode was covered with a white powder, and had lost 212 grains. Here again the two kinds of endosmose are perfectly distinct. But we have another curious result, viz. the muriatic acid apparently refusing to be transferred from the positive to the negative solution. This attracted particular attention, and the next experiment was conducted in the following manner:—100 grains of sulphate of copper were dissolved and put into a small porous vessel, the solution measuring $2\frac{1}{2}$ ounces; this was supported at the top of a deep glass vessel filled with dilute muriatic acid, so that several inches of solution were under the porous vessel, the surface of the two solutions being level; by this arrangement the copper salt formed at the positive electrode by the current sunk to the bottom by its own gravity and remained under the porous vessel, so that no transfer of salt could take

place. Two copper electrodes were used, and the current continued until the negative solution was exhausted of copper. When this was completed the negative electrode had gained in weight 25·1 grains: the solution had increased in measure half an ounce. On testing this by nitrate of silver, only a slight milkiness was obtained. The positive solution was deep blue at bottom, but only a slight tinge above the bottom of the porous vessel; the positive electrode was coated nearly to one-sixteenth of an inch with a white pasty matter, a great portion had also fallen to the bottom of the vessel: the electrode had lost in weight 132 grains. Here we have measurable endosmose amounting to half an ounce without any transfer of the acid in solution.

I now took two porous vessels, the one charged with $2\frac{1}{2}$ ounces by measure of a solution of sulphate of copper, the other with dilute muriatic acid; these were placed in a glass vessel filled with a measured quantity of distilled water, the cells placed 1 inch apart; two copper electrodes were used: the muriatic acid cell made the positive solution, the sulphate of copper the negative. A current from 9 pairs was kept up for eighteen hours. At first the decomposition was exceedingly slow, but it afterwards increased; the results of this experiment were—

Positive solution lost three-eighths of an ounce, pole covered with white powder, and had lost in weight 37 grains; solution contained sulphate of copper. The solution in the glass vessel was tinged blue by sulphate of copper, had lost in measure $1\frac{1}{2}$ ounce, and gave a copious precipitate with nitrate of silver, showing a transfer of muriatic acid from the positive cell.

The negative cell had increased in measure $1\frac{1}{4}$ ounce. Nitrate of silver gave no indication of muriatic acid, the electrode had increased in weight 26 grains.

A similar experiment was again repeated, the negative cell and glass vessel being both charged with distilled water, the positive with dilute muriatic acid; platinum electrodes were used. A 9-pair battery was attached for sixteen hours. The current passing was sufficient to keep deflected a galvanometer needle, but no evolution of gas was observed till nearly the end of the experiment, when the poles became covered with small bubbles of gas not large enough to be evolved. The results of this experiment were, positive cell lost in measure one-eighth of an ounce. The solution in the glass vessel was slightly acid, giving a precipitate with nitrate of silver, and had lost in measure $1\frac{1}{2}$ ounce. The negative cell had increased

in measure $1\frac{1}{2}$ ounce, did not change the colour of blue litmus paper, nor give any precipitate with nitrate of silver: here also, as in the last experiment, we have muriatic acid being transferred in small quantities from the positive to the intervening liquid. But another feature presents itself, the great amount of measurable endosmose and the almost entire absence of electrical decomposition; at the same time the endosmose being principally confined to the two vessels containing water, as if the acid in the cell had only acted the part of an electrode. On reversing the condition of the last experiment, the positive and glass vessel being charged with distilled water, the negative with the dilute muriatic acid, 9-pair battery, for sixteen hours, the positive vessel lost $1\frac{1}{2}$ ounce; the glass vessel had increased $1\frac{1}{4}$ ounce, while the negative or acid solution underwent no alteration, showing again the endosmose only between the two cells containing water.

Several experiments were repeated both with the single and double cells, having muriatic acid as the positive solution, with sulphate of copper, water and alkalies as the negative solution; in some I had transfer of acid in small quantity, in others no indication of transfer; I believe the cause of difference to be in the texture of the partition; when a diaphragm was used less porous, the endosmose was considerable, in one case amounting to 4 grains in thirty hours. Nitric and sulphuric acids, which are much more easily transferred than muriatic acid, have also had their transfer resisted by two closely-textured diaphragms, passing through one into the mid-division but not into the negative solution: however, these results show that all kinds of salts or acids are not transferred with the same facility, probably from their power of conduction.

While operating with the double cells, having an acid in the positive and water in the middle and negative cells, I have several times observed that both positive and negative solutions increased in bulk at the expense of the middle solution; in one instance the positive solution had gained 1 ounce, the negative gained three-fourths of an ounce, and the middle solution had lost $1\frac{3}{4}$ ounce. The negative and positive solutions originally contained only 2 ounces, the electrodes measured 2 by 1 inches; nevertheless in these instances the transfer of the acid from the positive to the negative was considerable. The different acids gave different results of this sort; with sulphuric acid the increase was greatest, muriatic acid one-half less, nitric acid about one-fourth of the sulphuric; whether this be the result of any fixed law I cannot say, the times I have ob-

served it being too few. As I have never observed these results except with the acids, I am inclined to think the cause to be what has been already stated, namely, the solution acting as the electrode, thus exposing a surface of acid to water in a state of excitement or tension sufficient to attract by its exalted affinity that fluid, and cause an increase of bulk in the cell, in a similar manner, as I shall endeavour to show in a forthcoming paper, to that which causes a greater amount of action at the positive electrode than at the negative in any electrolyte, and with muriatic acid and copper, as already referred to in a former part of this paper, amounting occasionally to five times that of the negative.

I shall now give the results, in a tabular form, of a few experiments made to determine the relation, if any, between the measurable endosmose and electrical decomposition.

The experiments were all made with the double cells of three compartments; the battery used being Wollaston's of 9-pair intensity; the time of each experiment was sixteen hours; the electrodes of platinum. The acids used were diluted as 1 to 25 water; solution of sulphate of copper the same strength in all.

| Positive solution. | Glass vessel (intermediate). | Negative solution. | Loss in positive. | Change in glass vessel. | Gain in negative. | Amount of deposit on decomposition. | Amount of measurable endosmose. |
|---|---|---|---|---|---|---|---|
| | | | Ounces. | Ounces. | Ounces. | Grains. | Ounces. |
| $SO^3$ | Water | Water | none | loss $\frac{1}{4}$ | $\frac{5}{8}$ | not measurable | $\frac{5}{8}$ |
| Water | Water | $SO^3$ | $\frac{1}{4}$ | none | $\frac{5}{8}$ | ..... | $\frac{5}{8}$ |
| $NO^5$ | Water | Water | $\frac{1}{4}$ | loss $\frac{1}{4}$ | $\frac{7}{8}$ | ..... | $\frac{7}{8}$ |
| Water | Water | $NO^5$ | 1 | gain $\frac{5}{8}$ | none | ..... | $\frac{5}{8}$ |
| HCl | Water | Water | $\frac{1}{8}$ | loss $1\frac{1}{4}$ | 1 | ..... | 1 |
| Water | Water | HCl | $1\frac{1}{2}$ | gain $1\frac{1}{4}$ | none | ..... | $1\frac{1}{4}$ |
| Water | Water | $SO^3CuO$ | $\frac{1}{4}$ | gain $\frac{1}{8}$ | $\frac{1}{8}$ | 1 | $\frac{1}{4}$ |
| Water | Water | $SO^3CuO$ | 1 | gain $\frac{1}{8}$ | $\frac{7}{8}$ | 10 | 1 |
| $SO^3CuO$ | $SO^3$ | $SO^3$ | $\frac{1}{10}$ | gain $\frac{1}{8}$ | $\frac{1}{8}$ | 33 | $\frac{1}{4}$ |
| $SO^3$ | $SO^3$ | $SO^3CuO$ | $\frac{5}{10}$ | gain $\frac{1}{2}$ | $\frac{1}{10}$ | 24 | $\frac{9}{10}$ |
| $SO^3CuO$ | Water | $SO^3$ | none | loss $\frac{1}{8}$ | $\frac{1}{4}$ | 11 | $\frac{1}{4}$ |
| $SO^3$ | Water | $SO^3CuO$ | $\frac{1}{2}$ | loss 1 | $1\frac{1}{2}$ | 30 | $1\frac{1}{2}$ |
| HCl | Water | $SO^3CuO$ | $\frac{2}{10}$ | loss $1\frac{2}{8}$ | $1\frac{1}{4}$ | 27 | $1\frac{1}{4}$ |
| $SO^3CuO$ | $SO^3CuO$ | $SO^3CuO$ | $\frac{1}{4}$ | loss $\frac{1}{10}$ | $\frac{1}{8}$ | 53 | $\frac{1}{8}$ |
| HCl | HCl | $SO^3Cu$ | $\frac{2}{10}$ | gain $\frac{1}{8}$ | $\frac{1}{10}$ | 43 | $\frac{2}{10}$ |
| $SO^3$ | Water | Water | gain $\frac{1}{2}$ | loss $\frac{3}{4}$ | $\frac{1}{4}$ | not measurable | $\frac{3}{4}$ |
| Water | Water | $SO^3$ | loss $\frac{5}{8}$ | loss $1\frac{1}{8}$ | 1 | evolution of gas | 1 |
| HCl | Water | Water | gain $\frac{1}{4}$ | loss $1\frac{3}{4}$ | 1 | not measurable | $1\frac{1}{4}$ |
| $NO^5$ | Water | Water | gain $\frac{1}{8}$ | loss $\frac{1}{8}$ | $\frac{1}{2}$ | not measurable | $\frac{5}{8}$ |
| $SO^3$ | Water | Water | loss $\frac{1}{8}$ | loss $\frac{3}{4}$ | $\frac{7}{8}$ | not measurable | $\frac{7}{8}$ |
| Common salt ... | Water | Water | none | loss 1 | 1 | not measurable | 1 |

The following table is of the same kind as the last, but the time of action and the power of the battery varying, as stated.

| Positive solution. | Solution of glass vessel. | Negative solution. | Loss in positive. | Change in glass vessel. | Gain in negative. | Amount of deposit. | Amount of measurable endosmose. | Time on. | Power of battery. |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Grs. | | hours | |
| $SO^3$ | $SO^3$ | $SO^3CuO$ | none | loss $\frac{1}{16}$ oz. | $\frac{1}{16}$ oz. | 21 | $\frac{1}{16}$oz | 2 | 2 p. large* pls. |
| HCl | HCl | $SO^3CuO$ | $\frac{1}{16}$ oz. | loss $\frac{1}{16}$ oz. | $\frac{1}{8}$ oz. | 12 | $\frac{1}{8}$ oz. | 2 | Ditto |
| $NO^5$ | $NO^5$ | $SO^3CuO$ | none | none | none | 23 | none | 2 | Ditto |
| HCl | HCl | $SO^3CuO$ | ... | ... | ... | 9 | ... | 2 | 2 p. small pls. |
| $SO^3$ | $SO^3$ | SO CuO | ... | ... | ... | 15 | ... | 2 | Ditto |
| $NO^5$ | $NO^5$ | $SO^3CuO$ | ... | ... | ... | 16 | ... | 2 | Ditto |
| $SO^3$ | $SO^3$ | $SO^3CuO$ | ... | ... | ... | 8 | ... | 2 | 1 p. large pls. |
| HCl | HCl | $SO^3CuO$ | ... | ... | ... | 7 | ... | 2 | Ditto |
| $NO^5$ | $NO^5$ | $SO^3CuO$ | ... | ... | ... | 8 | ... | 2 | Ditto |
| $SO^3$ | $SO^3$ | $SO^3CuO$ | ... | ... | ... | 6 | ... | 2 | 1 p. small pls. |
| HCl | HCl | $SO^3CuO$ | ... | ... | ... | 5 | ... | 2 | Ditto |
| $NO^5$ | $NO^5$ | $SO^3CuO$ | ... | ... | ... | 7 | ... | 2 | Ditto |
| CyK | CyK | $SO^3Cu$ | ... | loss $\frac{1}{4}$ oz. | $\frac{1}{8}$ oz. | 10 | $\frac{1}{4}$ oz. | 4 | Ditto |
| CyH | CyH | $SO^3CuO$ | $\frac{3}{4}$ oz. | gain $\frac{1}{4}$ oz. | $\frac{1}{4}$ oz. | 27 | $\frac{1}{2}$ oz. | 4 | 9 p. small pls. |

* In those marked large plates, the zinc plate of battery measured 6 by 4 inches; in those marked small, zinc measured 2 by $2\frac{1}{2}$ inches.

The result of these experiments, as well as those given before in detail, shows that there is no relation between the measurable endosmose and the amount of decomposition in the cells; so that the two phænomena must depend upon somewhat different causes, which now became an object of inquiry. Professor Faraday in his researches, mentions that a current of electricity may be made to pass through solutions without decomposing them, and Mr. Sturgeon gives it as his opinion that there is always an undecomposing current passing with a decomposing current. These observations being applied to the results of the present inquiry into measurable and unmeasurable endosmose, seemed to throw some light upon the distinct character of these phænomena, for, as will be observed, the measurable endosmose seems to be greatest when the current has the greatest difficulty to pass through, and when the decomposition is least; and on the contrary, the unmeasurable endosmose is greatest when the battery is powerful and the current passing freely, or rather decomposition going on freely.

In order to compare the two, I now tried a few experiments with different powers of battery, under constant circumstances as regards the decomposition cells. Each division of a decomposition cell had put into it 100 grains of sulphate of copper dissolved in 3 ounces of water; copper electrodes were used, and the current allowed to pass until the negative solution was exhausted of copper. The following is the mean of several trials.

With a 1-pair battery the negative solution exhausted in

forty-one hours, deposited upon pole 29 grains, being 3·4 grains more than the equivalent of 100 grains of sulphate, which is equal to 8·5 grains of sulphate which have passed by endosmose, not including water of crystallization, as I believe the salt passes without water. The negative solution had increased in bulk 1 ounce.

With a 2-pair battery the negative solution exhausted in nineteen hours, deposited upon pole 32 grains, being 6·4 grains more than the equivalent of 100 grains of sulphate, and equal to 16 grains of sulphate passed by endosmose. The solution had increased in bulk five-eighths of an ounce.

With a 4-pair battery the negative solution exhausted in twelve hours, deposited upon pole 35·6 grains, being 11 grains more than the equivalent of 100 grains of sulphate, and equal to 27·5 grains of sulphate passed by endosmose. The solution had increased half an ounce.

With a 6-pair battery the negative cell exhausted in seven hours, deposited upon pole 39 grains, being 14·4 grains more than the equivalent of 100 grains of sulphate, equal to 36 grains of sulphate passed by endosmose. The solution increased in bulk three-eighths of an ounce.

The two divisions of the decomposing cell were now charged with distilled water; two platinum electrodes were used; the current was also made to pass through a solution of sulphate of copper to ascertain if sufficiently strong to effect any decomposition; but in none of the experiments was any deposit obtained. Each experiment was continued thirty hours, when the cells stood thus:—

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| With one pair, | positive | lost | 1 | oz. | negative | gained | $\frac{5}{4}$ | oz. |
| ... two pairs | ... | ... | 1 | oz. | ... | ... | $\frac{5}{4}$ | oz. |
| ... four pairs | ... | ... | $1\frac{1}{4}$ | oz. | ... | ... | $\frac{7}{8}$ | oz. |
| ... six pairs | ... | ... | $1\frac{3}{8}$ | oz. | ... | ... | $1\frac{1}{8}$ | oz. |
| ... nine pairs | ... | ... | $1\frac{5}{8}$ | oz. | ... | ... | $1\frac{3}{8}$ | oz. |

With these, and all other experiments with water, a similar vessel to the decomposing cells was placed alongside, filled with water, to note the loss by evaporation, which in this case was three-eighths of an ounce, accounting for the loss in the two cells above.

A similar experiment was made with thirteen pairs of a Grove's battery, the current passed four hours; a gentle flow of gas was evolved from the electrode. No copper solution was used in this experiment. The cells stood thus: positive lost 2 ounces, negative gained $1\frac{3}{4}$ ounce.

The two divisions of the decomposition cell being again filled with distilled water, into one was put a piece of zinc and into the other a piece of platinum, connected by a wire;

in forty-eight hours the zinc cell had lost three-quarters of an ounce, the platinum cell had gained half an ounce. This experiment was repeated many times with similar results.

Two large cells were filled with distilled water, and a piece of zinc, measuring 4 by 6 inches, carefully weighed was put into one division and a piece of copper of the same size was put into the other division, the current passed through a delicate galvanometer, which kept deflected about 3°; the positive solution was kept at a given height, the negative was taken out as it increased, keeping the two solutions as nearly level as possible; this was kept up for forty days, when there was found to have passed through from the positive to the negative a bulk equal to 32 ounces, allowing for the evaporation, which was known by a similar vessel placed alongside. The zinc was covered with a gray film and had increased in weight 12 grains; this being carefully dissolved off by ammonia, water and the zinc again weighed, it was found to have lost 36 grains, which we may take as the amount of oxidation during the experiment.

The general conclusions which may be drawn from these experiments respecting endosmose are,

(1.) That the current of positive electricity passing through a liquid is always accompanied with a current of the liquid in the same direction.

(2.) If the liquid contains a salt or an acid that is undergoing decomposition, the endosmotic current is principally, if not wholly, confined to that salt or acid, unaccompanied with water, and therefore adds little or nothing to the bulk of the liquid into which it passes.

(3.) When the quantity of electricity which a battery is capable of giving off is greater than the salt or acid can conduct, the extra quantity, if we may so term it, passes through the water, taking with it, and thus inducing a flow of that liquid, into the negative cell, increasing the quantity; the same effect being produced with water when no salt or acid is in solution: hence the well-known fact, that endosmose is greatest with pure water, and even with currents that give no apparent decomposition, or rather a decomposition so minute as to be unobserved.

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## CLVII. *Analysis of a Cobalt Ore found in Western India.* By J. Middleton, *Esq., F.G.S., Principal of the Hon. East India Company's College at Agra.*

BEING engaged in analyses of the metallic ores of North-western India, with a view to the ascertainment of the constitutions of those most remarkable among them, and also

with the hope of detecting others whose existence in the country has not heretofore been even suspected, I am desirous of submitting to the Chemical Society the results of my inquiries whenever they appear to me of sufficient interest to justify my troubling them with them. I may mention, that should the Society desire any information from me on this or any other subject that I may be qualified and in a position to furnish, I shall most gladly meet their wishes.

The hilly districts of Rajpootanah are remarkably prolific inmetallic ores, many of these, too, exceedingly rich and abundant. Within a narrow compass in the independent state of Syepoore, are to be found the following minerals:—

Sulphuret of copper, sulphate of copper, sulphuret of cobalt, alum.

The native method of mining for the first of these ores, and which is the same as that adopted for the others, may be interesting to some of your members.

"The mine of copper is very deep, and difficult of access. The miners enter with burning lamps on their heads and with chisels, iron hammers, and baskets in their hands. They dig out the ore with their chisels by the light of their lamps, and bring it up with great labour and difficulty to the surface. They then pound and grind it small in a mill, after which they mix it with moist cow-dung, and this mixture being made into balls is placed in the sun to dry. When this has been accomplished the lumps are burnt, after which they are not broken up, but being mixed with an equal quantity of charcoal and as much iron filings, are put into a crucible, and a strong heat kept up by blowing with a leathern bellows till the dross separates and the copper settles at the bottom in the form of a solid disc. This product is again heated with charcoal until perfectly pure copper is produced*."

The mineral possessing greatest interest amongst those above enumerated is the sulphuret of cobalt. It is found in the copper mines in considerable abundance, and exists in a primitive schist in the form of bands and disseminated grains, the colour of which is a steel gray inclining to yellow. The grains appear to be crystallized, and are probably the cube and its derivatives. What is particularly remarkable in this ore is its purity, so far surpassing in this respect any that, so far as I am aware, is to be met with anywhere else. The only substance in combination with it, after separation of the matrix, is an iron pyrites, which is however but mechanically mixed, and so highly magnetic as to be readily removable by

* This description is the translation of a native one given to me with the minerals.

the magnet. The relative proportions in which these two exist are—

| | |
|---|---|
| Cobalt pyrites . . . . | 90·78 per cent. |
| Iron . . . . . | 9·22 ... |

The iron pyrites consists of black amorphous granules without metallic lustre, and, as above stated, it is highly magnetic, having at the same time the low specific gravity of 2·58. It gives on analysis—

| | |
|---|---|
| Iron . . . . . | 62·27 per cent. |
| Sulphur . . . . . | 37·73 ... |

The analysis was carefully made, and repeated for verification, so that, notwithstanding the specific gravity is so much lower than that assigned as characteristic of iron pyrites, there can be no doubt such is the constitution of this constituent of the ore in question.

The cobalt pyrites exhibits the usual characteristic reactions, generally subject to some modifications, which do not deserve notice, as I found them to be mostly owing to the high temperature at which my experiments were made: one however is rather remarkable, and not assignable to this cause, but probably to the particular natural constitution of the mineral, which, as I have found, in other cases modifies the behaviour of substances occasionally.

Ferrocyanide of potassium produces in acid solutions a bluish-green precipitate, which completely dissolves up in forty-eight hours, provided the solution be not highly concentrated, to a brilliant emerald-green fluid, which is not affected by acids or by standing, but the colour of which changes to greenish yellow, without precipitation, by ammonia.

By very careful and repeated analysis, the reduction process having been adopted for the metal, I found the proportion of the constituents to be, taking the average,—

| | |
|---|---|
| Cobalt . . . . . | 64·64 per cent. |
| Sulphur . . . . . | 35·36 ... |

from which it is obvious the substance is a sub-sulphuret, that its constitution is $Co_2 S$, a rather remarkable result, considering that the iron compound, doubtless of simultaneous formation, is different.

The cobalt pyrites has the specific gravity of 5·45. It is used by Indian jewellers for staining gold of a delicate rose-red colour; the *modus operandi* which they follow I have been unable to learn; it is a secret with them, which they are unwilling to disclose.

## CLVIII. *Notes on the Preparation of Alloxan.* By William Gregory, *M.D., F.R.S.E.*

IN an interesting and able paper on alloxan and its derivatives, the first part of which appears in Liebig's *Annalen* for September 1845, Schlieper enters into minute details concerning the most advantageous method of preparing alloxan, and after describing the results which he obtained on repeating the process given by me, proposes a new method of his own, which he considers in every way preferable, as yielding, with greater facility and certainty, a larger proportion of alloxan. Professor Liebig in his Lectures (Lancet 1845) also recommends Schlieper's method as the best in every respect.

I am still, notwithstanding, inclined to give a decided preference to my own process, when carefully performed, and that on the grounds of its superior simplicity, facility and productiveness. A brief comparison of the two methods, with their results, will enable the reader to judge for himself.

I must first of all, however, observe, that Schlieper, in repeating my process, has not obtained results so favourable as I had formerly announced; so that, in his hands, his own method has been the more productive. I formerly obtained from 100 parts of uric acid 90 of crystallized (hydrated) alloxan, perfectly pure, not reckoning the portion of alloxan remaining in the mother-liquids. Schlieper, on the other hand, from 15 ounces of uric acid, treated by my process, obtained, including the contents of the mother-liquids, 8 ounces hydrated alloxan, $1\frac{3}{4}$ ounce alloxantine ($= 2\frac{1}{4}$ ounces alloxan), and $\frac{3}{4}$ ounce parabanic acid; in all equivalent to about $11\frac{1}{4}$ ounces of alloxan. This only amounts to 75 per cent.; whereas I obtained 90 per cent., exclusive of the mother-liquids, which I find on an average to yield fully one-tenth more; in all, therefore, at least 100 per cent. I may here state that I have never failed to obtain this as an average result since my process was published, although I have very often repeated the process. Several of my pupils have been equally successful. I shall now, therefore, describe the process as I have for some time pursued it, and its simplicity will, I trust, be evident.

In my original account of this process, I recommended the use of nitric acid of sp. gr. 1·3 to 1·35, and it was with such acid, as I believed, that my results were obtained. But as Schlieper found it impossible to succeed with acid of less sp. gr. than 1·4 to 1·42, I suspect that I may have been mistaken as to the sp. gr. of my acid. This I cannot now ascertain; but it is rendered probable by the circumstance that, in the experiments about to be mentioned, I found an acid of

1·412 to answer my purpose perfectly, with the same appearances as I had formerly observed.

Schlieper having corrected this error proceeds to describe my process, as performed by him, with great accuracy and minuteness, and his description of the phænomena entirely agrees with my experience. I can only account for his not obtaining such favourable results as I have always done, to the circumstance of his acid being a little too concentrated. However this may be, on reading his paper I proceeded to repeat my process, and obtained the results to be hereafter stated.

The following is the process I now follow:—2 or $2\frac{1}{2}$ fluid ounces of colourless nitric acid, sp. gr. 1·412, are placed in a flat-bottomed dish or beaker glass, and as much uric acid is introduced as will lie on the point of a small spatula. This is well-stirred in to prevent the formation of lumps, and in a few minutes effervescence commences, the liquid becomes slightly warm, and the powder dissolves. More uric acid is now added, taking care never to exceed a certain small quantity, and not to allow the liquid to become warm beyond a certain degree, which is easily judged of by laying the dish on the hand. If too hot when uric acid is added, or if too much acid be added at once, the uniform steady effervescence is changed into a violent and tumultuous action, after which no alloxan can be obtained. It is proper to have a plate with cold water at hand, in which to place the dish or glass if it should seem likely to become too warm. But a little practice enables us to regulate the operation so that no external cooling is required.

After several portions of uric acid have been added, crystals of alloxan begin to appear in the warm liquid, but the addition of uric acid is to be continued, with the same precautions, till so much alloxan has been formed, that on cooling the whole becomes nearly semisolid. When this point is reached the liquid has become somewhat viscid, and this, along with the presence of the crystalline deposit of alloxan, gives a peculiar character to the effervescence toward the end of the operation. I commonly find that with $2\frac{1}{2}$ fluid ounces of nitric acid the point above alluded to is reached when about 1200 grains of uric acid dried at 212° have been dissolved. It does not answer to operate on a much larger scale; it is better to use several dishes at once, each containing $2\frac{1}{2}$ or at the most 3 fluid ounces of acid. For every 500 grains of uric acid 1 fluid ounce of nitric acid may be allowed.

The whole is now allowed to stand all night in a cool place, and next day the alloxan is collected on a funnel with the aid of a little asbestus. The mother-liquid drains off, and the

last portions of it are cautiously displaced by ice-cold water, till the droppings are found to have only a moderately strong acid taste. The alloxan on the funnel, which is anhydrous, is then digested with just as much water at 140° or 150° F. as will dissolve it. The solution is filtered, and on cooling deposits a large crop of crystals of hydrated alloxan. [Should too much water have been added, the filtered liquid must be evaporated at from 120° to 140° F., till on cooling it crystallizes abundantly.] The mother-liquid of these crystals, evaporated at the same temperature, yields a second crop. The mother-liquor of this is added to the acid mother-liquor previously drained off, and the whole liquid treated, after the addition of two or three times its bulk of water, with sulphuretted hydrogen, till the alloxan present is reduced to the state of alloxantine. As a part is always reduced still further to dialuric acid, the liquid must be exposed to the air for a day or two, or until it deposits no more crystals. The alloxantine is purified by solution in boiling water, filtration to separate sulphur, and crystallization; and when dry three parts of it correspond to rather more than four of hydrated alloxan. If required, it may very easily be converted into alloxan; as Schlieper has described this process I need not repeat it here.

The mother-liquid of the alloxantine generally yields some parabanic acid; but very little if the process has been carefully performed.

I think it will be admitted that the above process is sufficiently simple. It will be observed that I no longer recommend the separation of the alloxan formed from the nitric acid in several successive portions, but that there is only one operation for all, in which the alloxan is collected on a funnel with asbestus. I used sometimes to divide the process into five successive operations, and generally made three of them: but I am now convinced that it is best to dissolve in the nitric acid the whole of the uric acid that is to be dissolved before collecting the alloxan.

Let us now consider the productiveness of this method. I have already stated my average of former results to have been 90 per cent. of crystallized alloxan, exclusive of the mother-liquid, which corresponded to one-tenth more. As the process now stands we have—1. The first crop of crystals of alloxan, varying with the proportion of water used to dissolve the anhydrous alloxan. 2. The second crop of the same crystals. 3. The alloxantine from the mother-liquid converted into alloxan, or calculated in that form. I take no account of the parabanic acid.

*Experiment* 1.—Uric acid 2600 grains; alloxan, first crop,

1950 grains, second crop, 550 grains; alloxantine, 200 grains, equivalent to alloxan, 290 grains. In all, therefore, from 2600 grains of uric acid, 2790 grains of hydrated alloxan, or 107 per cent. nearly.

*Experiment* 2.—Uric acid, 1130 grains; alloxan, first crop, 800 grains, second crop, 140 grains; alloxantine, 80 grains, equivalent to alloxan, 116 grains. In all, therefore, 1056 grs. of alloxan from 1130 of uric acid, or 93 per cent.

*Experiment* 3.—Uric acid, 1500 grains; alloxan, first crop, 1150 grains, second crop, 270 grains; alloxantine, 120 grains, equivalent to alloxan, 174 grains. In all, therefore, from 1500 grains of uric acid, 1594 grains of alloxan, or 106 per cent.

The above results, averaging 102 per cent. of pure hydrated alloxan, were obtained without difficulty. Indeed the only delicate point in the process is the attention necessary to avoid too great a rise in temperature, alloxan being decomposed by heat even when simply dissolved in water, but still more when acid is present. A little experience however makes this quite easy; and besides, this difficulty attaches equally to Schlieper's new method, as we shall see.

The formula of uric acid being $C_{10}\ N_4\ H_4\ O_6$, while that of hydrated alloxan is $C_8\ N_2\ H_4\ O_{10} + 6$ aq, it is obvious that 100 parts of uric acid can produce about 128 of alloxan. It is not likely that we shall ever obtain the full proportion without loss, but I consider my process, simple as it is, to furnish a very satisfactory approximation, considering the impossibility of separating the whole alloxan from the acid liquid in which it is formed.

If we now refer to Schlieper's account of his new method, we find that it includes the following operations:—1. The uric acid is acted on by hydrochloric acid and chlorate of potash, care being necessary, as in my process, to keep the temperature below a certain point. 2. The *whole* of the alloxan is reduced by sulphuretted hydrogen to the state of alloxantine. 3. The alloxantine is reoxidized by nitric acid, and thus reconverted into alloxan. I cannot admit that this process is either more simple or more easy than my own. On the contrary, as I obtain nine-tenths of the whole alloxan, or 90 parts from 100 of uric acid directly as alloxan, and pure, in the first crystallizations, while Schlieper first converts all his alloxan into alloxantine, and then reconverts the alloxantine into alloxan; and further, as I use no other reagent but nitric acid in preparing these nine-tenths, the advantage of simplicity and facility is entirely on my side.

From 4 ounces of uric acid, Schlieper obtains by his own

process 2 ounces 7 drachms and 20 grains of alloxantine, equivalent theoretically to 3 ounces and 7 drachms of alloxan, or nearly 97 per cent. But in reconverting this alloxantine into alloxan by nitric acid, it will be found impossible to obtain, practically, the whole alloxan, since some of it must remain in the mother-liquid; and moreover, in the process of oxidation by heating with nitric acid some alloxan is very likely to be converted into parabanic acid, and thus lost. Judging from experience, I should not expect the 97 per cent. of alloxan obtained in theory to yield, in crystals, more than 90 per cent.

As far as productiveness, therefore, is concerned, I may claim also a superiority for my method. It is true that it has not succeeded so well in the hands of Schlieper, but this must I think be attributed to accidental causes, and possibly to a want of perfect familiarity with the method on the part of Schlieper, who seems to be so good an operator, that I cannot doubt that he would, after a little practice, obtain the same results as I have always succeeded in obtaining.

Finally, I beg to remind those who may wish to try my process, that what Schlieper describes as a modification of my process is the process itself, unmodified; because the only change introduced by Schlieper consists in the use of acid at 1·4 or 1·42 instead of 1·3 or 1·35, as erroneously recommended in my original process. In point of fact, the acid which I have long used for the purpose has the sp. gr. 1·412, and for this number 1·3 or 1·35 was accidentally substituted in writing or printing my former notice. In common with all chemists I am much indebted to M. Schlieper for pointing out this oversight.

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January 5, 1846.—The President in the Chair.

The Proceedings of the Glasgow Philosophical Society, from 1842 to 1845, presented by the Society.

The Bakerian Lecture for 1845, by Dr. Daubeny, presented by the author.

The following papers were read :—

Professor Graham described a new eudiometric process for the rapid absorption of oxygen gas from atmospheric air and other gaseous mixtures containing oxygen. It consists in the employment of a solution in ammonia of a sulphite of the suboxide of copper and ammonia. This salt falls as a granular powder, when a stream of sulphurous acid gas is conveyed into a cold solution of the ammoniacal sulphate of copper. When dissolved in ammonia it absorbs oxygen with singular avidity, and when employed in this form in eudiometry gives results of considerable uniformity.

## CLIX. *On the unequal Decomposition of Electrolytes, and the Theory of Electrolysis.* *By* Mr. James Napier.

IN a paper which I submitted to the Society last session upon this subject*, it was mentioned that the fundamental law laid down by electro-chemists, "That there can be no inequality of decomposition in any part of an electrolyte," is not applicable under all circumstances, especially when the negative element of the electrolyte can combine with the positive electrode, there being under such circumstances an increased tendency in the electrode to combine with the electrolyte, which causes a greater amount of decomposition or chemical action at the positive than at the negative electrode.

That the extra amount of decomposition at the positive electrode is not the result of the ordinary solvent powers of the electrolyte for the metal composing the electrode, was shown by pieces of the same metal being put into the same solutions as the electrolyte the same length of time as the battery was in action, and which were in some cases not affected, and in others only a small fraction of that which had taken place at the positive electrode above what the current of electricity passing accounted for; showing that the increased affinity between the elements of the electrolyte and the electrode had its origin in some influence communicated by the battery, and was not accounted for by the amount of electricity passing, measured by the deposition of a metal upon the negative electrode, and as experiments which were being made showed, without any relation to that current.

I had observed, while experimenting upon electrical endosmose, that there seemed some relation between the cause of measurable endosmose and the phænomenon under consideration: it became therefore probable that the element of an electrolyte liberated at the negative pole, such as a deposited metal, might not be, as I had formerly thought, an accurate measure of the whole electricity passing through the solution under all circumstances, but that a feeble current may be also passing, which may be sufficient to give a greater disposition, if I may be allowed the term, to the solid electrode to combine with the elements of the electrolyte, but not of sufficient power to decompose all the particles of the compound fluid through which it passes to the negative electrode, the solution conducting it as a solid conductor would, or rather, as appears from the results described in my paper on

* See vol. ii. p. 255.

endosmose, the electricity taking the dissolved particles with it to the negative electrode and producing the phænomena of endosmose. These suppositions therefore became the object of an inquiry, which I shall now describe in detail.

I took a piece of amalgamated zinc, measuring 2 by $2\frac{1}{2}$ inches, in such state of amalgamation that dilute sulphuric acid had no action upon it; this was put into a mixture of sulphuric acid and water in the proportion of 1 acid to 24 water, and surrounded with copper, which was placed as close to the zinc as would allow a free current of the solution between them, as well as the escape of gas, with the view of interrupting as little as possible the free action of the acid upon the zinc. This was kept in action for an hour, when it was found that the zinc had dissolved from it 97 grains. This I assumed as the maximum amount of chemical action which could be obtained between the zinc and acid of this strength, at least under the influence of copper. The zinc and copper being again put into this liquid, but with the two metals 1 inch apart, connected by a slip of copper at the surface of the liquid, in one hour there was dissolved from the zinc 56·5 grains. The two metals being again placed in the same position, but connected by two copper electrodes of equal size placed into a solution of sulphate of copper, at the expiration of an hour there was deposited upon the negative electrode 9 grains of copper, and there were dissolved from the zinc 10·7 grains. Taking another zinc and copper and putting them into the acid connected with the first in the manner practised for intensity, there were deposited in one hour 17 grains. The zinc in cell had lost 18 grains. With 4 pairs zinc and copper in acid there were deposited 26 grains, and dissolved from the zinc 27·7 grains. With 6 pairs there were deposited 34 grains, and dissolved from zinc 36 grains; and with 9 pairs there were deposited 43 grains, and dissolved from the zinc 45 grains. And thus it went on increasing in quantity by the addition of plates until the action of the acid and zinc came nearly to the same as was assumed as a maximum, namely, 97 grains; with 30 pairs there were dissolved from zinc 101 grains, with 35 pairs 99, which I consider very close to the assumed quantity.

Assuming the position which the results of these experiments suggest, I would say, that if the chemical energy induced between the acid and zinc under the influence of copper be equal to 100 grains per hour, but by distance or the interposition of a medium of inferior conducting power the chemical action is reduced to 10 grains per hour, the remaining tendency or disposition of the acid and zinc to unite

will be equal to 90; and by increasing the action, either by adding intensity or decreasing the resistance, so that it amounts to 25 grains per hour, we decrease the tendency to further action to 75, and so on, the one decreasing as the other increases. Now, if this tendency for further action between the acid and zinc be the source of this feeble or undecomposing current, and this the cause of an extra chemical action at the positive over the negative electrode, then the amount of this extra action at this locality will be greatest with a weak battery, at least have some relation to the surface of zinc exposed and the amount of actual chemical action going on. That this is the case the following experiments will show. To save repetition, I may state that when small plates are mentioned the measures of the zinc are 2 by $2\frac{1}{2}$ inches; when large plates are named they measure 5 by 6 inches.

1. With small plates, the electrodes being the same size as plates, both placed in sulphate of copper with a very little free acid. The current passing four hours, the results were as under:—

| | | | | | |
|---|---|---|---|---|---|
| One pair negative gained | 27 grs. | | Positive lost | 30·5 grs. | |
| Two pairs | ... | 44 ... | ... | 49 | ... |
| Four pairs | ... | 58 ... | ... | 63 | ... |
| Six pairs | ... | 70 ... | ... | 73 | ... |
| Nine pairs | ... | 85 ... | ... | 87 | ... |

Taking these results in equivalent proportion, counting the equivalent of copper 32, the extra action at positive will be—

| | |
|---|---|
| One pair . . . . . | 4·1 grains. |
| Two pairs . . . . . | 3·6 ... |
| Four pairs . . . . . | 2·7 ... |
| Six pairs . . . . . | 1·3 ... |
| Nine pairs . . . . . | 0·7 ... |

The next experiment was with cyanide of potassium in the proportion of 1 ounce to the pint of water. This was put into one division of a decomposition cell, the other being charged with sulphate of copper; silver positive electrodes were used in the cyanide solution. The battery used was of small plates, the current passing two hours.

| | | | | | |
|---|---|---|---|---|---|
| One pair negative gained | 14 grs. | | Positive lost | 57 grs. | |
| Two pairs | ... | 14 ... | ... | 50 | ... |
| Four pairs | ... | 20 ... | ... | 70 | ... |
| Six pairs | ... | 21 ... | ... | 71 | ... |

The equivalent of deposit being again taken, the proportions of extra solution of positive stand thus:—

| | |
|---|---|
| One pair . . . . . | 9·1 grs. |
| Two pairs . . . . . | 6·8 ... |
| Four pairs . . . . . | 5·7 ... |
| Six pairs . . . . . | 0·9 ... |

I now took a strong solution of cyanide of potassium and divided it into three equal parts: into two were placed porous vessels filled with sulphate of copper, in which were put the negative electrode of the battery, one connected with 9 pairs of small plates, the other with 1 pair of large plates. The same sort of electrodes were used in both experiments. The third portion of cyanide of potassium solution had a piece of copper placed in it of the same size with the electrodes. The battery current was continued one hour. The results were—

9 pairs deposited 12 grains, dissolved 15 grains; equivalent 8 grains.

1 pair deposited 4 grains, dissolved 7 grains; equivalent 24 grains.

Piece of metal in cyanide potassium lost 1·2 grain.

Similar experiments were made with various electrolytes in the positive division, using sulphate of copper in all cases in the negative, the amount deposited being taken as the measure of the decomposing current.

1st. Positive cell charged with a weak solution of cyanide of potassium.

1 pair deposited 7 grains, dissolved 10 grains; equivalent proportion 13·7 grains.

9 pairs deposited 26 grains, dissolved 31 grains; equivalent proportion 6·1 grains.

2nd. Muriatic acid 1 to 24 water in positive solution.

1 pair deposited 15 grains, dissolved 23 grains; equivalent 17 grains.

9 pairs deposited 54 grains, dissolved 69 grains; equivalent 8·8 grains.

3rd. Positive solution, nitric acid 1 to 24 water.

1 pair deposited 17 grains, dissolved 20 grains; equivalent 5·6 grains.

9 pairs deposited 26 grains, dissolved 29 grains; equivalent 3·7 grains.

4th. Positive solution, sulphuric acid 1 to 24 water.

1 pair deposited 20 grains, dissolved 23 grains; equivalent 4·3 grains.

9 pairs deposited 49 grains, dissolved 55 grains; equivalent 3·9 grains.

The next series of experiments are of the same kind, using

1 and 2 pairs of large and small plates; but two porous vessels were used, put into a vessel charged with the same liquid as the positive, the negative in this, as in the last, being charged with sulphate of copper, the electrodes being 2 by $2\frac{1}{2}$ inches in all the experiments.

1st. Positive solution, sulphuric acid 1 to 24 water.

1 pair small plates deposited 9 grains, dissolved 11 grains; equivalent 7 grains.

1 pair large plates deposited 9 grains, dissolved 12 grains; equivalent 10·6 grains.

2 pairs small plates deposited 16 grains, dissolved 18 grains; equivalent 4 grains.

2 pairs large plates dissolved 19 grains, dissolved 22 grains; equivalent 5 grains.

2nd. Positive solution, muriatic acid 1 to 24 water.

1 pair small plates deposited 5 grains, dissolved 6 grains; equivalent 6·3 grains.

1 pair large plates deposited 7 grains, dissolved 9 grains; equivalent 9·1 grains.

2 pairs small plates deposited 9 grains, dissolved 12 grains; equivalent 9·4 grains.

2 pairs large plates deposited 11 grains, dissolved 16 grains; equivalent 14·5 grains.

3rd. Positive solution, nitric acid 1 to 24 water.

1 pair small plates deposited 8 grains, dissolved 9 grains; equivalent 4 grains.

1 pair large plates deposited 8 grains, dissolved 10 grains; equivalent 8 grains.

2 pairs small plates deposited 14 grains, dissolved 15 grains; equivalent 2·3 grains.

2 pairs large plates deposited 19 grains, dissolved 21 grains; equivalent 3·3 grains.

I now took three separate pairs of small plates excited by 1 sulphuric acid to 24 water, and to each attached copper electrodes, which were placed in a solution of sulphate of copper: the electrodes of one were one-half size of the battery plates, of the other equal size, and of the third twice the size of the battery plates. The current passed sixteen hours, the results were as follows:—

Small negative electrode gained 25·4 grains, positive lost 29·3 grains; equivalent 4·9 grains.

Equal-sized negative electrode gained 33 grains, positive lost 37 grains; equivalent 3·8 grains.

Large negative electrode gained 42 grains, positive lost 44 grains; equivalent 1·5 grain.

A piece of zinc and copper, each measuring 3 inches by 3, were placed in distilled water, and two small electrodes, 1 by 2 inches, attached and placed in a solution of sulphate of copper. The current passing was sufficient to deflect a delicate galvanometer needle 3°: the current was allowed to pass seventy-two hours. The electrodes being again weighed, the negative had undergone no change, the positive had lost 2·6 grains.

Another experiment of the same kind, but the electrodes placed in dilute sulphuric acid, 1 to 100 water, the current passed forty-eight hours; the negative electrode was found unchanged, the positive had lost 2 grains. A piece of copper suspended in the acid solution during the same time remained unchanged.

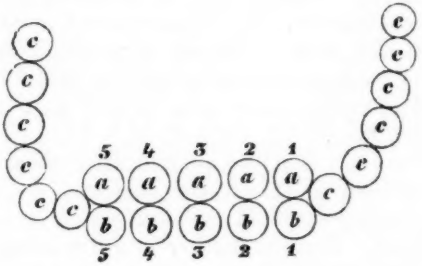
These experiments, which are only a few of a great many that were made, all bearing more or less on the point, I think sufficiently prove the view taken both of the origin of the undecomposing current of electricity, and also that it is that current which produces the phænomenon under discussion; namely, a disposition in the positive electrode and in the zinc in the battery to combine with the negative element of the electrolyte up to a given point, varying according to the strength of acid, and the negative properties, if we may so term it, of the metal in contact with the zinc, through the influence of which the chemical action is induced.

The results of the experiments of this as well as my preceding paper upon electrical endosmose, are applicable to the explanation of various natural and chemical phænomena, the investigations into some of which I am at present engaged with. At present I shall confine myself to a few remarks upon the philosophy of electrolytic action which these experiments suggest.

The manner in which electricity passes through and decomposes solutions, is a subject that has occupied the attention of electro-chemists since its power to do so was first known, and the opinions published are almost as numerous as the investigators; the greater part of which having been already collected and published by Professor Faraday in his Fifth Series of Researches, need not be repeated here. Suffice it to say, that the whole of these theories being based upon the supposition that there is a mutual transfer of both the negative and positive elements of an electrolyte, and that supposition being now found incorrect, these theories cease to be tenable.

From the first time that I observed that the base of an electrolyte was not transferred, my mind became impressed with

a theory of electrolytic action, which seemed to agree with the results of my every-day experience in electro-metallurgy, and also with various experiments made on a small scale, in order to test these views more fully. During these trials I was favoured with a copy of the paper of the late Professor Daniell and Professor Miller on the decomposition of secondary compounds, in which the non-transfer of the basic element is observed, but the statement made at the same time that this is not universal, some elements, such as potassium, sodium, &c., being transferred in certain proportions. These statements interfering with my views, induced me to investigate the subject more closely. The paper now submitted to the Society forms a portion of these investigations, the results of which induces me to think it probable that the results obtained by these gentlemen were due to what I term unmeasurable endosmose rather than to electrolytic transfer; and that no basic element of an electrolyte is ever transferred by electrolytic action, but that the base of an electrolyte which is being decomposed is the medium or conductor of the electricity through the solution from electrode to electrode. And the manner in which this takes place I conceive to be as follows:—




The double row represents a line of compound atoms forming an electrolyte, *a* the acid or negative element of the electrolyte, *b* the base or positive element of the electrolyte, *c c* the wires or solid conductors of the electricity from the battery to the decomposition cell; the last particles in contact with the electrolyte may be viewed as the electrodes. The *a b* particles are held together by their affinity for each other.

Now let it be supposed that an equivalent of electricity leaves the positive terminal of the battery and passes along the solid particles of the conductor, that particle upon which the electricity rests must be for the time in a higher state of excitement than the other particles. When the electric current comes to the last particle of the solid chain which is in contact

with the electrolyte, its increased excitement causes it to attract and combine with the acid particle nearest it, *a* 1; when these unite the electricity passes to the first basic particle *b* 1, giving it an exalted excitement, which causes it to unite with the acid particle *a* 2, the electric force passing to *b* 2, which becomes excited in turn and takes the particle *a* 3; and so on through the chain till the last particle *b* 5, which, having no further acid to combine with, gives its electricity to the solid conductor which passes along to the battery. If the last particle *b* 5 be a metal that can exist under the circumstances in which it is left, such as copper, silver, &c., it accumulates upon that electrode as a deposit; if not such as can exist under these circumstances, such as potassium, &c., it decomposes water and hydrogen is evolved. By this we observe that every equivalent of decomposition will carry an equivalent of acid to the positive electrode. This is exactly what is found by experiment to be the case. That these decompositions and combinations amongst the particles of a salt may produce a current of that salt in the direction of the electric current producing endosmose, can very easily be conceived.

Whether this be the true philosophy of electrolytic action is yet to be further investigated; in the mean time it does not appear inconsistent with any experiments I have yet investigated: but should it be found not to account for electrolytic action under all circumstances, it will be gratifying should it only prove a stepping-stone to a clearer view of the subtile action of this power.

It appears to me that the phænomena observed and described in these papers favour the idea that electricity is but one power or substance, and that that power is identical with chemical affinity. But the further consideration of this point must be deferred till another opportunity.

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January 19, 1846.—James Lowe Wheeler, Esq., in the Chair.

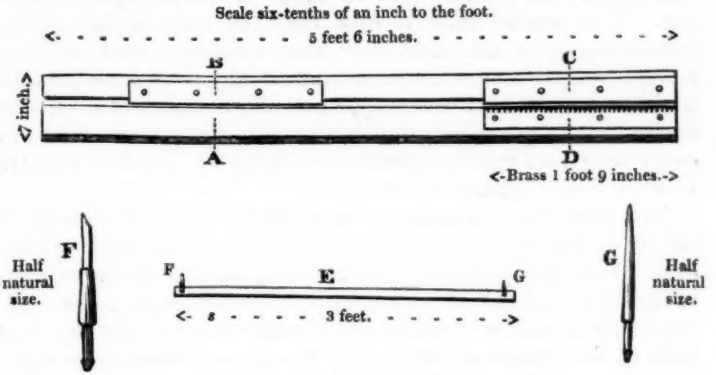
Mr. Button presented specimens of Paraffine, Naphthaline, and Anhydrous Phosphoric Acid to the Society's Museum.

The following communication was read:—

## CLX. *On a convenient Instrument for graduating Glass Tubes.*

DR. PLAYFAIR described an instrument for graduating tubes, invented by Professor Bunsen of Marburg, and used in the researches on the gases from iron furnaces, and in the late experiments read to the Society on specific gravity.

It consists of a mahogany board $5\frac{1}{3}$ feet long, 7 inches wide, three-quarters of an inch thick. Throughout its centre is a groove 1 inch wide, half an inch deep, arched at bottom, for the reception of tubes. At one part, 5 inches from the end, is placed a brass plate, $1\frac{1}{3}$ foot long and 2 inches wide, in such a position that when screwed down its edge comes one-half over the groove. It is furnished with 4 screw-nuts, passing through a cut portion of the plate, a quarter of an inch long, so as to allow a certain advancement or withdrawal




of the plate at pleasure. C and D are two similar plates, placed at the other end of the wooden board, C having the same amount of motion as B, and being precisely similar in every respect. D is a brass plate of the same dimensions as B and C, but the screws go through a hole of the same size as themselves into the wood. It is cut, at intervals of five millimetres, into notches, every alternate one being one-twentieth and one-tenth of an inch deep. The instrument is provided with a wooden rod, 3 feet long, 1 inch broad, and half an inch thick, E. This is provided with two steel points, placed by screws at half an inch from either end. One of these, F, is in the form of a knife, the other, G, of a bradawl. The instrument is furnished with a screw-driver, that these may be removed at pleasure.

When a tube is to be graduated, it is covered with a thin layer of melted wax and turpentine, by means of a camel's-hair pencil, and is placed in the groove between C and D, which are then screwed down in their places, so as to retain the tube firmly in its position. A standard tube, previously mathematically divided into millimetres (the most convenient division), is now placed in the groove under B, which is then screwed upon it. The rod E is now used, the pointed steel

G being put in one of the millimetre marks on the standard tube; the knife-formed steel F is now upon the waxed tube, and is made to make a mark upon it, the length of which is regulated by the distance between the edges of C and D. The pointed steel is now removed back one millimetre on the standard tube, and the corresponding mark made on the waxed one; and thus we proceed until the whole of the waxed tube is divided into millimetres. The object of the notches is, that a longer mark may be made at every five millimetres, and a still longer one at every ten, in order to aid the eye in reading. The waxed tube is now removed to a leaden chest, containing pounded fluor spar and sulphuric acid, slightly heated, which etches it more successfully than a solution of hydrofluoric acid. Previously, however, to being etched, it is desirable to figure the number of millimetres at the space of every ten; and this is conveniently done by the steel pointer G after being removed from E.

We have thus an accurate measure of length etched upon the tube, which should have been one of pretty uniform calibre. The next point is to determine the true value of each of the divisional marks. This is done by calibrating it throughout all its length with small portions of mercury, say equal in bulk to five grains of water. By this means the relative value of each mark may be determined, and the proportion which it bears to any given standard. The only possible error is in the assumption that the tube is of even calibre between the space occupied by the mercury; but the quantity of this added is so small that any such error becomes quite inappreciable.

The convenience of this graduator is so great, that a long tube may be beautifully divided in the course of a quarter or half an hour. The standard tubes should be made of glass, but the original divisions from which this standard is made may be made on wood or any other material.

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February 2, 1846.—The President in the Chair.

Isaac Solly Lister, Esq. was elected a Member of the Society.

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February 16, 1846.—Wm. Thomas Brande, Esq., Vice-President, in the Chair.

Mr. Button presented a specimen of Succinate of Ammonia.

Dr. Wilson presented his Essay "On the employment of Oxygen Gas as a means of Resuscitation in Asphyxia."

Mr. James Napier was re-elected an Associate Member of the Society.

The following papers were read:—

Mr. J. C. Nesbitt described an improved method of detecting alumina. The process depends on the insolubility of the phosphate of alumina in acetic acid, and the two following experiments will show the advantages of this test:—

1st. Two grs. of alum were dissolved in 1000 grs. of water, and a single drop of this solution was mixed with a little solution of phosphate of soda, to which acetate of ammonia and acetic acid had been added; in a few minutes a precipitate of phosphate of alumina was produced.

Another drop was mixed with ammonia, and the usual tests were employed to detect alumina, but no precipitate was produced.

Some ordinary solution of potash was mixed with a strong solution of muriate of ammonia. The mixture showed no change after the lapse of two days.

Another portion of the same solution of potash was mixed with a solution of muriate of ammonia, containing a few drops of solution of phosphate of soda. A precipitate was produced in the course of twenty minutes or half an hour.

In order to detect alumina in the ashes of plants, or in substances containing similar ingredients, it is merely necessary to precipitate the oxide of iron (if any be present) and the alumina as phosphates, by the addition, if necessary, of phosphate of soda, acetate of ammonia and acetic acid. This precipitate is to be boiled with a solution of pure caustic potash; the phosphate of alumina will be dissolved, and may be again precipitated by muriate or acetate of ammonia and acetic acid.

## CLXI. *Researches on Atomic Volume and Specific Gravity.* By Lyon Playfair, *Esq., Ph.D. and* J. P. Joule, *Esq.*

### Series II.—*On the relation in volumes between simple bodies, their oxides and sulphurets, and on the differences exhibited by Polymorphous and Allotropic substances.*

IN our former memoir we gave a sketch of the progress of discovery in this branch of scientific research, but we unintentionally omitted the name of Dumas. Pierre's* interesting memoir has clearly shown that, twenty years since, the French chemist pointed out the fact that isomorphous groups possess the same atomic volume, and various chemists, amongst whom we have already cited Thomson, Kopp, Schröder and Persoz, afterwards cultivated the same field. The purpose of our former memoir was to point out that the volumes of salts are related to each other by simple laws, and in the communication which we have now the honour to present to the Society, it is our object to extend, confirm, and simplify our views to other solid substances. The correct expression

* Millon and Reiset, *Annuaire de Chemie* for 1846.

of a law is not generally attained at its first discovery, although the truth of the law may be sufficiently indicated. In our present memoir we do not treat of substances in solution, our object being to confirm the multiple relation which we have already pointed out in the case of solid salts, and to exhibit the connexion between the two units 9·8 and 11·0 which we then assumed as the sub-multiples.

We commence with the volumes of the metallic elements, which are to a certain extent well-suited for a correct estimation of specific gravity. But at the same time it must be borne in mind, that the force of cohesion exercises upon them an influence so strong, as to make their exact density depend upon the circumstances under which they are examined. Thus iridium, possessing, after fusion, the sp. gr. 20·0, affects only 16·0 when obtained by the reduction of its oxide; and osmium under similar circumstances possesses respectively the specific gravities 19·50 and 10·0. The effect of hammering certain metals is also well-known to be a means of increasing their density. These points must be kept in view in considering the results obtained by experiment; for they obviously indicate that the force of cohesion is able to diminish the natural volumes which the metals would otherwise enjoy.

In most cases it was unnecessary for us again to determine the density of the metals, as that has frequently formed a subject of special examination. But since the more recent discoveries in electricity furnish the means of procuring metals in a state of greater purity than formerly, we have occasionally availed ourselves of this power, in order to obtain results of the most unexceptionable character. In such cases the metal was precipitated upon a platinum wire of known weight, and after removing it from the liquid in which precipitation was effected and washing it with distilled water, the wire with the adhering metal was plunged into strong alcohol, then wrapped in bibulous paper and allowed to remain in a warm place until the smell of alcohol had disappeared. By this means the surface was preserved perfectly clear and untarnished, which is not the case in the ordinary modes of drying. The specific gravity was then determined by the usual hydrostatic method, care being taken to use recently boiled water for the purpose of removing the air adhering to the metal. The temperature of observation is always understood to be 40°.

The specific gravity of the oxides and sulphurets was taken in an instrument similar to that described in our first memoir (page 405), but susceptible of much greater accuracy. In our former instruments, as we stated, we only measured to the tenths of a grain, in those used in our present researches

we could read off with the greatest facility the hundredth part of a grain. This improvement was effected by using tubes of a smaller bore, and graduating them with the instrument invented by Professor Bunsen. The capacity of the instrument was determined at 40°, the temperature of the maximum density of water, and all our estimations in the present memoir refer to this temperature. Turpentine was used as the liquid in the volumenometer, and it was restored to precisely the same temperature as at the commencement of the experiment by immersing the instrument in water.

## Section I.

### *Specific Gravities and Volumes of Metallic Elements.*

*Manganese*, Mn = 27·7.—Bergmann states the sp. gr. of this metal as 6·861 and 7·1. But the later estimations of John and Bachmann being uniform deserve a preference: the former gives its sp. gr. as 8·013, the latter as 8·030. The volume of the equivalent is therefore as follows:—

| | | Mean. |
|---|---|---|
| I. Mn volume | = 3·46 | 3·455 |
| II. ... | = 3·45 | |

*Iron*, Fe = 28·0.—According to Brisson the specific gravity of this metal is 7·788, according to Karsten 7·790. The volume according to both results is 3·59.

*Cobalt*, Co = 29·5.—The specific gravity of this metal has engaged the attention of various chemists, and the following results have been obtained:—

8·513 Berzelius.
8·558 T. H. Henry*.
8·485 Brunner.
8·500 Mitscherlich.
8·538 Haüy.

The mean of these results, 8·519, gives 3·46 as the atomic volume.

*Nickel*, Ni = 29·5.—There are various determinations of the specific gravity of this metal in a fused state.

7·807 Brisson.
8·279 Richter.
8·402 Tourte.
8·380 Tupputi.
8·637 Brunner.
8·477 Baumgartner.

* Upon a well-fused button weighing 171 grains and determined at our request by Mr. Henry.

The mean result, 8·33, gives the volume of the equivalent 3·54.

*Zinc*, Zn = 32·3.—The following specific gravities are recorded by Berzelius and Brisson, to which we add the result of one of our own experiments on an electrotype specimen, of which a detailed account will be found as we proceed.

6·862 Berzelius.
6·861 Brisson.
6·869 P. and J.

The mean result, 6·864, gives 4·71 as the volume of zinc.

*Cadmium*, Cd = 55·8.—The following specific gravities are the most uniform of those recorded with regard to this metal:—

8·659 Herapath.
8·635 Karsten.
8·604 Stromeyer.
8·670 Children.

The mean result, 8·642, gives the volume 6·46.

*Copper*, Cu = 31·60.—Our estimations of the specific gravity of this metal agree closely with those of other experimenters.

8·830 Berzelius.
8·900 Herapath.
8·721 Karsten.
8·895 Hatchett.
8·884 P. and J.
8·941 P. and J.

The mean of these results, 8·862, gives a volume for the equivalent of 3·56.

*Chromium*, Cr = 28·0.—Two estimations exist of the specific gravity of this metal. Richter states it to be 5·90, Thomson makes it 5·1. The mean, 5·5, gives as the volume 5·09.

*Aluminium*, Al = 13·72.—Wöhler has lately given the specific gravity of this metal, determined on small quantities, as 2·5 and 2·67. Adopting the latter number as most likely to be nearest the truth, we have the atomic volume 5·13.

*Bismuth*, Bi = 71·07.—The following estimations are selected as being the most uniform:—

9·670 Musschenbroek.
9·654 Karsten.
9·822 Brisson.
9·831 Herapath.
9·882 Thenard.
9·800 Leonhard.

The mean result, 9·776, yields the volume 7·27.

*Tin*, Sn = 58·90.—The specific gravities recorded by various observers are uniform and agree with the density of a beautiful specimen which we prepared by precipitation.

7·291 Kupffer.
7·290 Karsten.
7·291 Brisson.
7·295 Musschenbroek.
7·285 Herapath.
7·248 P. and J.

The mean of these results, 7·283, indicates the volume 8·09 for the equivalent of tin.

*Arsenic*, As = 75·4.—The specific gravity of this metal seems to vary under certain circumstances, as the results obtained by different observers deviate considerably from each other.

5·763 Brisson. Stromeyer.
5·884 Turner.
5·959 Guibourt.
5·700 Guibourt.
5·672 Herapath.
5·628 Karsten.
5·766 Mohs.

The mean, 5·767, yields the volume 13·07; but, if we select the two estimations by Karsten and Herapath the mean sp. gr. will be 5·65 and atomic vol. 13·35.

*Antimony*, Sb = 129·20.—The following observers have determined the specific gravity of this metal:—

6·712 Hatchett.
6·733 Boeckmann.
6·702 Brisson.
6·852 Musschenbroek.
6·860 Bergmann.
6·610 Breithaupt.
6·700 Karsten.
6·646 Mohs.

The mean result, 6·727, gives the volume of the equivalent 19·21.

*Molybdenum*, Mo = 47·96.—According to Bucholz, the specific gravity of this metal is 8·615 and 8·636. Hielm states it at 7·500, a number obviously too low. The mean result of the former chemist gives 8·625 as the specific gravity and 5·56 as the volume of the equivalent.

*Tungsten*, W = 94·8.—D'Elhuyart describes the specific gravity as 17·60; Bucholz as 17·40; Allan and Aiken as

17·22. The mean of these results gives 17·40 as the specific gravity of the metal, and 5·45 as the volume of the equivalent.

*Titanium*, Ti = 24·30.—Wollaston describes the specific gravity as 5·3, Karsten as 5·28. The mean result, 5·29, gives the atomic volume as 4·59.

*Tellurium*, Te = 64·2.—The following are the recorded specific gravities of this metal:—

6·115 Klaproth.
6·138 Magnus.
6·343 Reichenstein.
6·258 Berzelius.
6·130 Berzelius.

The mean result, 6·196, gives 10·36 as the atomic volume.

*Lead*, Pb = 103·6.—The specific gravities recorded are as follows; we also add two estimations by ourselves:—

11·207 Boeckmann.
11·352 Herapath.
11·352 Brisson.
11·330 Kupffer.
11·388 Morveau.
11·388 Karsten.
11·445 Musschenbroek.
11·275 P. and J.
11·298 P. and J.

The average specific gravity, 11·337, gives 9·14 as the atomic volume.

*Mercury*, Hg = 101·43.—The specific gravity of solid (frozen) mercury is stated by Kupffer and Cavallo to be about 14·0, which makes the atomic volume 7·24.

*Silver*, Ag = 108.—According to Brisson the specific gravity of this metal is 10·474, according to one of our own experiments 10·522; the mean result, 10·498, gives 10·29 as the atomic volume.

*Gold*, Au = 199·2.—Brisson describes the specific gravity as 19·258, which gives the atomic volume 10·34.

*Platinum*, Pt = 98·8.—Brisson states the specific gravity of this metal to be 20·98, a result which is nearly the mean of all the specific gravities recorded. The atomic volume is therefore 4·71.

*Palladium*, Pd = 53·3.—Breithaupt describes the specific gravity of a chemically pure specimen as 10·923, a result closely agreeing with the observations of Cloud and Wollaston. The atomic volume must therefore be 4·88.

*Rhodium*, R = 52·2.—Cloud took the specific gravity of a

specimen fused by the oxyhydrogen blowpipe and found it to be 11·2. Wollaston states it at 11·0. The mean, 11·1, gives the atomic volume 4·7.

*Osmium*, Os = 99·7.—The specific gravity of the metal, as obtained by the reduction of its oxide with hydrogen, is 10·0; this gives the atomic volume 9·97.

*Iridium*, Ir = 98·84.—The following are the recorded specific gravities of this metal, neglecting the determination of Berzelius, which will afterwards come under special consideration.

19·50 Mohs.
18·68 Children.
23·55 Breithaupt.
22·11 Breithaupt.

The mean result, 20·96, gives 4·71 as the atomic volume.

*Potassium*, K = 39·15.—According to Gay-Lussac and Thenard the specific gravity of this metal is 0·865; its atomic volume is therefore 45·26.

*Sodium*, Na = 23·3.—Gay-Lussac and Thenard describe the specific gravity of sodium as 0·972. Davy states it at 0·935. The mean, 0·953, yields the atomic volume 24·45.

*Barium*, Ba = 68·7.—The specific gravity of barium is about 4·0, according to Davy; hence its atomic volume would be 17·17.

*Strontium*, Sr = 43·8.—Gehler states the specific gravity to be between 4·0 and 5·0. The mean, 4·5, yields the atomic volume 9·73.

In the previous part of this paper all the metals are included the specific gravities of which have been determined with any degree of certainty. An inspection of the numbers representing their atomic volumes will show the existence of a decided multiple relation. In our former paper we represented 9·8, the volume of ice, as a primitive volume for salts*. This number, however, must be made up of the numbers representing the volumes of oxygen and hydrogen respectively. The number 9·8 cannot itself represent the primitive volume, but a certain sub-multiple of it may do so. A little consideration of the results now detailed shows that this sub-multiple is the number 1·225, or the eighth part of the volume of ice — $\frac{9{\cdot}8}{8} = 1{\cdot}225$. The divisor 8 is the cube of 2, so that the atom of ice (considered as a globe or cube) will have exactly twice the linear dimensions of the atom possessing the volume 1·225. It will however

* That number being deduced from the sp. gr. 0·9184 determined by us, a number almost identical with that recently found by Brunner, 0·918.

be observed that in several cases the above volumes correspond more exactly to the multiple of a volume of $\frac{1{\cdot}225}{2} = {\cdot}6125$. But as $\frac{1{\cdot}225}{2}$ is rather an exceptional than a general bulk, the convenience in illustration of the law of multiple proportions will be considerable, if in the mean time we assume 1·225 as the standard number for comparison. We do not state it as the absolute unit, but as a general and convenient standard bulk for illustrating the law of multiple proportions.

TABLE I.—Showing the Atomic Volumes and Specific Gravities of the Metallic Elements.

| Designation. | | Volume and specific gravity. | | | | |
|---|---|---|---|---|---|---|
| Name. | Atomic weight. | Vol. by experiment. | 1·225 or $\frac{1}{8}$ vol. of ice as standard for comparison. | Volume by theory. | Sp. gr. by experiment. | Sp. gr. by theory. |
| Manganese | 27·7 | 3·455 | 3 | 3·67 | 8·021 | 7.547 |
| Iron | 28·0 | 3·59 | 3 | 3·67 | 7·789 | 7·629 |
| Cobalt | 29·5 | 3·46 | 3 | 3·67 | 8·519 | 8·038 |
| Nickel | 29·5 | 3·54 | 3 | 3·67 | 8·33 | 8·038 |
| Copper | 31·6 | 3·56 | 3 | 3·67 | 8·862 | 8·610 |
| Aluminium | 13·72 | 5·13 | 4 | 4·9 | 2·67 | 2·80 |
| Zinc | 32·3 | 4·71 | 4 | 4·9 | 6·864 | 6·590 |
| Cadmium | 55·8 | 6·46 | 5 | 6·12 | 8·642 | 9·117 |
| Chromium | 28·0 | 5·09 | 4 | 4·9 | 5·500 | 5·714 |
| Bismuth | 71·07 | 7·27 | 6 | 7·35 | 9·776 | 9·669 |
| Tin | 58·90 | 8·09 | $6\frac{1}{2}$ | 7·96 | 7·283 | 7·400 |
| Arsenic | 75·40 | 13·07 | 11 | 13·47 | 5·767 | 5·597 |
| Antimony | 129·20 | 19·21 | 16 | 19·6 | 6·727 | 6·591 |
| Molybdenum | 47·96 | 5·56 | $4\frac{1}{2}$ | 5·51 | 8·625 | 8·704 |
| Tungsten | 94·8 | 5·45 | $4\frac{1}{2}$ | 5·51 | 17·40 | 17·205 |
| Titanium | 24·30 | 4·59 | 4 | 4·9 | 5·29 | 4·959 |
| Tellurium | 64·2 | 10·36 | $8\frac{1}{2}$ | 10·41 | 6·196 | 6·167 |
| Lead | 103·6 | 9·14 | $7\frac{1}{2}$ | 9·18 | 11·337 | 11·285 |
| Mercury | 101·43 | 7·24 | 6 | 7·35 | 14·000 | 13·800 |
| Silver | 108·0 | 10·29 | $8\frac{1}{2}$ | 10·41 | 10·498 | 10·375 |
| Gold | 199·2 | 10·34 | $8\frac{1}{2}$ | 10·41 | 19·258 | 19·135 |
| Platinum | 98·8 | 4·71 | 4 | 4·9 | 20·98 | 20·163 |
| Palladium | 53·3 | 4·88 | 4 | 4·9 | 10·923 | 10·877 |
| Rhodium | 52·2 | 4·70 | 4 | 4·9 | 11·100 | 10·657 |
| Osmium | 99·7 | 9·97 | 8 | 9·8 | 10·00 | 10·173 |
| Iridium | 98·84 | 4·71 | 4 | 4·9 | 20·960 | 20·171 |
| Potassium | 39·15 | 45·26 | 37 | 45·32 | 0·865 | ·863 |
| Sodium | 23·30 | 24·45 | 20 | 24·50 | 0·953 | ·951 |
| Barium | 68·70 | 17·17 | 14 | 17·15 | 4·000 | 4·005 |
| Strontium | 43·80 | 9·73 | 8 | 9·8 | 4·50 | 4·469 |

The table exhibits clearly a simple multiple relation with-

out however giving precise accordance between the theoretical and experimental results in many of the metals*. This want of accordance might either be due to the force of cohesion, which prevents the metals assuming their natural volumes, or it might be owing to the unlike conditions and impurity in the specimens operated upon. To determine these points we instituted the following experiments on simple bodies.

In order to render our conclusions still more worthy of attention, we have repeated the estimation of many specific gravities, carefully guarding against any impurity in the substances under examination as well as any irregularity in their crystalline condition. In the case of the metals, no method appeared to us more likely to give unexceptionable results than that of crystallizing them from their solutions by electricity. By this means we have obtained the specific gravity of silver, copper, zinc, lead, and tin as follows :—

*Specific gravity of Silver.*—A solution of the cyanide of silver was furnished with two electrodes, viz. a plate of silver and a piece of fine silver wire, the former being in connexion with the positive, the latter with the negative end of a single constant cell of Daniell's arrangement. After five or six days, we found that the fine silver wire was covered to a considerable thickness with a beautiful crystalline deposit of silver of the most perfect whiteness. Having carefully washed the silver, we suspended it by an excessively fine platinum wire to the hydrostatic scale of a very excellent balance, and weighed it in distilled water of the temperature of 40°. We then carefully dried it and weighed it in air.

| | |
|---|---|
| Weight in water at 40° . . | 84·41 grains |
| Weight in air . . . . . | 93·26 ... |
| Sp. gr. reduced to a vacuum | 10·537 |

* In the case of alloys, where the cohesion is diminished, the results generally are very exact, and the coincidence in many cases strikingly identical with the theoretical expression. Thus $Sn_2Pb$ has, according to Regnault, a sp. gr. 8·777, according to Kupffer 8·637, mean 8·707. $\frac{221\cdot4}{8\cdot707} = 25\cdot42$, V being the unit vol. 1·225.

$$Snv \times 2 + Pbv = 25\cdot10.$$

Sn Pb has, according to Regnault, sp. gr. 9·387, according to Kupffer 9·436, mean 9·411. $\frac{162\cdot5}{9\cdot411} = 17\cdot26$.

$$Snv + Pbv = 17\cdot15.$$

Again, St $Pb_2$ has, according to Kupffer, sp. gr. 10·078. $\frac{266\cdot1}{10\cdot078} = 26\cdot40$,

$$Snv + Pbv \times 2 = 26\cdot33.$$

Another similar experiment gave us the following results:—

| | |
|---|---|
| Weight in water at 49° . . | 122·93 grains |
| Weight in air . . . . . | 135·84 ... |
| Sp. gr. reduced to water at 40°. | 10·522 |

| | | |
|---|---|---|
| I. | Sp. gr. of silver | 10·537 |
| II. | ... | 10·522 |
| | Mean . . | 10·530 |

*Specific gravity of Copper.*—A piece of sheet copper was employed as the negative element of a Daniell's cell for three or four days, due care being taken to supply the cupreous solution with fresh crystals of sulphate of copper from time to time. The electrotype copper having been detached and washed, was then weighed in distilled water at 49°; and then again, after drying, in air.

| | |
|---|---|
| Weight in water . . . . | 149·07 grains |
| Weight in air . . . . . | 167·97 ... |
| Sp. gr. reduced. . . . . | 8·884 |

A second experiment conducted in the same way, gave—

| | |
|---|---|
| Weight in water . . . . | 261·10 grains |
| Weight in air . . . . . | 293·97 ... |
| Sp. gr. reduced. . . . . | 8·941 |

In a third experiment, we found—

| | |
|---|---|
| Weight in water at 44° . . | 264·508 grains |
| Weight in air . . . . . | 297·838 ... |
| Sp. gr. reduced. . . . . | 8·934 |

| | | |
|---|---|---|
| I. | Sp. gr. of copper | 8·884 |
| II. | ... | 8·941 |
| III. | ... | 8·934 |
| | Mean . . | 8·920 |

*Specific gravity of Zinc.*—A saturated solution of pure sulphate of zinc was furnished with electrodes of zinc, and placed in connexion with a battery consisting of three Daniell's cells. In about twenty-four hours a good plate of tough zinc was deposited on the negative electrode. The plate was weighed in water which had been previously boiled in order to prevent its acting on the zinc.

| | |
|---|---|
| Weight in water . . | 181·14 grains |
| Weight in air . . . | 212·00 ... |
| Reduced sp. gr. . . | 6·869 |

In a second experiment we obtained—

| | |
|---|---|
| Weight in water . . | 161·14 grains |
| Weight in air . . . | 188·02 ... |
| Reduced sp. gr. . . | 6·992 |

A third experiment gave—

| | |
|---|---|
| Weight in water . . | 176·53 grains |
| Weight in air . . . | 206·16 ... |
| Reduced sp. gr. . . | 6·956 |

| | | |
|---|---|---|
| I. | Sp. gr. of zinc | 6·869 |
| II. | ... | 6·992 |
| III. | ... | 6·956 |
| | Mean . . | 6·939 |

*Specific gravity of Lead.*—A very fine platinum wire was made negative (by means of a single constant cell) in a saturated solution of acetate of lead; a plate of lead formed the positive electrode. In about twenty hours a most beautiful lead-tree was formed on the platinum wire. The wire with its leaden foliage was then carefully removed from the solution, well-washed in hot water, and weighed in distilled water at 54° which had been recently boiled to remove carbonic acid gas. The fine platinum wire upon which the lead was deposited served as the means of suspension on the hydrostatic scale. Lastly, the lead was carefully removed from the water, immersed in alcohol, wrapped up in bibulous paper, and put on a warm stove to dry. By thus operating the lead was dried without losing much of its brilliancy. A very small correction had to be applied for the platinum wire which weighed 0·3 of a grain.

| | |
|---|---|
| *Exp.* 1.—Weight in water at 54° . . | 74·74 grains |
| Weight in air . . . . . | 82·00 ... |
| Sp. gr. reduced to water at 40° and to a vacuum . . . . | 11·275 |
| *Exp.* 2.—Weight in water at 60° . . | 62·80 grains |
| Weight in air . . . . . | 69·03 ... |
| Sp. gr. reduced . . . . | 11·070 |
| *Exp.* 3.—Weight in water at 54° . . | 64·92 grains |
| Weight in air . . . . . | 71·22 ... |
| Sp. gr. reduced . . . . . | 11·298 |
| *Exp.* 4.—Weight in water at 62° . . | 62·82 grains |
| Weight in air . . . . . | 68·92 ... |
| Sp. gr. reduced . . . . | 11·280 |

| | | |
|---|---|---|
| I. | Sp. gr. of lead | 11·275 |
| II. | ... | 11·070 |
| III. | ... | 11·298 |
| IV. | ... | 11·280 |
| | Mean . . | 11·231 |

*Specific gravity of Tin.*—The experiments with tin were made in a manner exactly similar to those with lead, a solution of chloride of tin being employed. The branching crystals of this metal were of extreme beauty.

| | | |
|---|---|---|
| *Exp.* 1.— | Weight in water . . . | 35·74 grains |
| | Weight in air . . . . | 41·46 ... |
| | Reduced sp. gr. . . . | 7·245 |
| *Exp.* 2.— | Weight in water . . . | 36·35 grains |
| | Weight in air . . . | 42·06 ... |
| | Reduced sp. gr. . . . | 7·363 |
| *Exp.* 3.— | Weight in water . . . | 40·58 grains |
| | Weight in air . . . . | 46·99 ... |
| | Reduced sp. gr. . . . | 7·330 |
| *Exp.* 4.— | Weight in water . . . | 34·063 grains |
| | Weight in air . . . . | 39·477 ... |
| | Reduced sp. gr. . . . | 7·288 |

| | | |
|---|---|---|
| I. | Sp. gr. of tin | 7·245 |
| II. | ... | 7·363 |
| III. | ... | 7·330 |
| IV. | ... | 7·288 |
| | Mean . . | 7·306 |

There are several other metals which we have not yet tried, and others, as for example, iron, which we have not been able to deposit in a satisfactory state; but the instances we have given are, we think, sufficient to show that the specific gravities of the electrotype metals are not widely different from those obtained in the usual way. And therefore while we claim a superior degree of accuracy to our results with the electrotype metals, we think that if a law be established for the volumes of the metals it will be indicated with tolerable accuracy by the results obtained in the ordinary way.

*Specific gravity of Sulphur.*—A quantity of flowers of sulphur was melted in a glass vessel; and after a crust had formed on the surface on cooling, the remainder was poured off. The crystals of sulphur, weighing 79·07 grains, were then thrown into a specific gravity bottle partly filled with water. The bottle with its contents was slightly warmed and then boiled under the exhausted receiver of an air-pump in order to remove the air which is so liable to adhere to sulphur. The bottle was then filled up with water, reduced to a known

temperature, and weighed. The weight of the bottle when filled with pure water at 50½° being 644·22 grains, and its weight when filled at the same temperature with water and 79·07 grains of sulphur being 683·97, it follows that 39·32 grains of water were displaced by the sulphur.

Weight of water displaced by 79·07 grs. of sulphur = 39·32 grains.

Sp. gr. of the crystals, 2·010.

*Specific gravity of Platinum Sponge.*—The experiments with this substance were conducted in exactly the same manner as that with sulphur.

*Exp.* 1.—Weight of water displaced by 109·02 grains of platinum sponge . . . . . = 5·15 grains
Sp. gr. of the metal . . . 21·169

*Exp.* 2.—Weight of water displaced by 107·32 grains of platinum sponge . . . . . = 5·052 grains
Sp. gr. of the metal . . . 21·243

I. Sp. gr. of platinum sponge 21·169
II. ... 21·243
Mean . . . . 21·206

*Specific gravity of Phosphorus.*—Weight of water displaced by 44·76 grains of phosphorus = 24·87 grains.

Sp. gr. of phosphorus, 1·800.

TABLE II.—Showing the Volumes of Metals and some other Simple Bodies.

| Designation. | | Volume. | | | | | |
|---|---|---|---|---|---|---|---|
| Name. | Atomic weight. | Volume by experiment. | Vol. increased by $\frac{1}{20}$th. | 1·225 or $\frac{9·8}{8}$ as unity. | Volume by theory. | Sp. gr. by experiment. | |
| Silver | 108·3 | 10·285 | 10·799 | 9 | 11·025 | 10·530 | Our own experiments. |
| Copper | 31·65 | 3·548 | 3·725 | 3 | 3·675 | 8·920 | |
| Zinc | 32·31 | 4·656 | 4·889 | 4 | 4·900 | 6·939 | |
| Lead | 103·73 | 9·236 | 9·698 | 8 | 9·800 | 11·231 | |
| Tin | 58·92 | 8·064 | 8·467 | 7 | 8·575 | 7·306 | |
| Sulphur | 16·03 | 7·975 | 8·373 | 7 | 8·575 | 2·010 | |
| Platinum | 98·84 | 4·661 | 4·894 | 4 | 4·900 | 21·206 | |
| Phosphorus | 31·44 | 17·470 | 18·343 | 15 | 18·375 | 1·800 | |
| Iron | 28·0 | 3·590 | 3·769 | 3 | 3·675 | 7·800 | Various authorities. |
| Nickel | 29·62 | 3·420 | 3·591 | 3 | 3·675 | 8·660 | |
| Antimony | 64·62 | 9·420 | 9·891 | 8 | 9·800 | 6·860 | |
| Solid Mercury | 101·43 | 7·245 | 7·607 | 6 | 7·350 | 14·000 | |
| Gold | 99·6 | 5·107 | 5·362 | 4½ | 5·512 | 19·500 | |
| Palladium | 53·36 | 4·640 | 4·872 | 4 | 4·900 | 11·500 | |
| Diamond | 12·00 | 3·478 | 3·651 | 3 | 3·675 | 3·450 | |

The volumes given in the above table are evidently in a simple multiple ratio with themselves, and by adding one-twentieth they all come nearly into the category of the number 1·225. Whether the contracted state of the metals in the solid state be owing to the attraction of cohesion we have not examined. We think it highly probable however that if the volumes were reduced to the zero of temperature and compared with ice, also at the zero, they would be found in a strictly correct multiple ratio. The coefficients of dilatation which we have examined seem to favour this view, as also does the high rate of the expansion of ice found by Brunner; as however we have not yet made many experiments on the dilatation of solid bodies by heat, we prefer deferring the consideration of this point to future communications.

*Specific gravity of Metals in a finely divided state.*

Under the impression that the contracted state of the metals in their usual solid condition was in a great measure owing to the attraction of cohesion, we now entered with great interest upon the examination of metals obtained by reducing their oxides by hydrogen gas. In these experiments we employed a specific gravity bottle, on account of the facilities which it presented in the case of those metals which ignite on exposure to air.

*Specific gravity of Copper obtained by reducing the Oxide.*—A stream of dried hydrogen gas was transmitted through a tube of German glass heated to redness and containing oxide of copper. After the reduction seemed to be quite completed, the operation was carried on a quarter of an hour longer in order to prevent the slightest trace of oxide being left. The tube with its contents having cooled, the copper was removed, pounded into small fragments, weighed, and thrown into a specific gravity bottle partly filled with water. This done, the bottle with its contents was slightly warmed and then placed under the exhausted receiver of an air-pump, in order to boil away any air that might possibly lodge among the lumps of metal. The bottle was then filled up with water and placed in a dish of water in order to reduce it to a given temperature. The perforated stopper was then inserted and the bottle dried and weighed. The weight of the bottle, when filled with water only, being known, it was easy to find the quantity of water displaced by the copper in the manner described in the experiment with sulphur already cited.

*Exp.* 1.—Weight of water displaced by

| | |
|---|---|
| 212·6 grains of copper . | = 25·22 grains |
| Sp. gr. reduced . . . . . | 8·428 |

*Exp.* 2.—Weight of water displaced by
156·8 grains of copper . . 18·48 grains
Sp. gr. reduced . . . . . 8·483

*Exp.* 3.—Weight of water displaced by
199·55 grains of copper . 23·865 grains
Sp. gr. reduced . . . . . 8·360

| | | |
|---|---|---|
| I. | Sp. gr. of copper | 8·428 |
| II. | ... | 8·483 |
| III. | ... | 8·360 |
| | Mean . . | 8·424 |

*Specific gravity of Cobalt obtained by reducing the Oxide.*—The experiments with this metal were conducted in a similar manner to those with copper, except that turpentine was employed in the specific gravity bottle instead of water, and that the metal was weighed in the tube in which it was obtained, and shaken into the bottle with as little exposure to the air as possible. On account of the great expansion of turpentine it was necessary to take particular care in reducing the bottle to a given temperature. The specific gravity of the turpentine was found to be 0·8764 at 40°.

*Exp.* 1.—Weight of turpentine displaced
by 52·5 grains of cobalt . . 5·57 grains
Sp. gr. referred to water at 40° 8·260

*Exp.* 2.—Weight of turpentine displaced
by 65·26 grains of cobalt . 7·41 grains
Sp. gr. referred to water at 40° 7·718

| | | |
|---|---|---|
| I. | Sp. gr. of cobalt | 8·260 |
| II. | ... | 7·718 |
| | Mean . . | 7·989 |

*Specific gravity of Nickel obtained by reducing the Oxide.*—The experiments with this metal were conducted precisely as those with cobalt.

*Exp.* 1.—Weight of turpentine displaced
by 91·58 grains of nickel . 10·1 grains
Sp. gr. . . . . 7·861

*Exp.* 2.—Weight of turpentine displaced
by 70·28 grains of nickel . 7·81 grains
Sp. gr. . . . . 7·803

| | | |
|---|---|---|
| I. | Sp. gr. of nickel | 7·861 |
| II. | ... | 7·803 |
| | Mean . . | 7·832 |

*Specific gravity of Iron obtained by reducing the Peroxide.*

| | |
|---|---|
| Weight of turpentine displaced by 46·7 grains of iron . . . . . | 7·52 grains |
| Sp. gr. . . . . | 7·130 |

*Specific gravity of Arsenic obtained from Arsenietted Hydrogen at a low temperature.*

| | |
|---|---|
| Weight of turpentine displaced by 1·031 grains of arsenic . . . . . | 0·171 grains |
| Sp. gr. . . . . | 5·230 |

*Specific gravity of Flowers of Sulphur.*—The sulphur having been thrown into a specific gravity bottle, a small portion of water was added to it, and the bottle well-shaken so as to cause the sulphur to be thoroughly wetted. The bottle was then placed under the exhausted receiver of an air-pump so as to remove the air lodging in the sulphur. Then more water was added and the same operation repeated. When at last we were satisfied that the sulphur was entirely deprived of air, we filled the remainder of the bottle with water, reduced it to a known temperature, and weighed it.

| | |
|---|---|
| *Exp.* 1.—Weight of water displaced by 158·2 grains of sulphur . . | 82·82 grains |
| Sp. gr. reduced to water at 40° | 1·910 |
| *Exp.* 2.—Weight of water displaced by 167·12 grains of sulphur . | 87·22 grains |
| Sp. gr. reduced . . . . . | 1·916 |

| | | |
|---|---|---|
| I. | Sp. gr. of flowers of sulphur | 1·910 |
| II. | ... ... | 1·916 |
| | Mean . . | 1·913 |

*Specific gravity of Platinum obtained by exposing the Oxide to a bright red heat.*

| | |
|---|---|
| Weight of water displaced by 111·92 grains of platinum . . . . . | 6·3 grains |
| Sp. gr. . . . . | 17·766 |

This does not differ much from the specific gravity 17·890 of the same body, as obtained by Scholz.

*Specific gravity of Uranium obtained by Wöhler's method.*

| | |
|---|---|
| Weight of turpentine displaced by 65·475 grains of uranium . . . . . | 6·74 grains |
| Sp. gr. . . . . | 8·425 |

*Specific gravity of Magnesium.*—The specimen examined was prepared and presented to one of us by Professor Liebig.

*Exp.* 1.—Weight of turpentine displaced by 5·235 grains of magnesium . . . . . 2·033 grains
Sp. gr. . . . . 2·233

*Exp.* 2.—Weight of turpentine displaced by 4·144 grains of magnesium . . . . . 1·60 grains
Sp. gr. . . . . 2·246

I. Sp. gr. of magnesium 2·233
II. ... 2·246
Mean 2·240

TABLE III.—Showing the Volumes of several Metals in a finely divided state and that of Flowers of Sulphur*.

| Designation. | | Volume. | | | | |
|---|---|---|---|---|---|---|
| Name. | Atomic weight. | Volume by experiment. | 1·225 as unity. | Volume by theory. | Sp. gr. by theory. | Sp. gr. by experiment. |
| Copper ..... | 31·65 | 3·757 | 3 | 3·675 | 8·612 | 8·424 |
| Cobalt..... | 29·57 | 3·701 | 3 | 3·675 | 8·047 | 7·989 |
| Nickel..... | 29·62 | 3·782 | 3 | 3·675 | 8·060 | 7·832 |
| Iron ..... | 27·18 | 3·812 | 3 | 3·675 | 7·396 | 7·130 |
| Arsenic ..... | 37·67 | 7·203 | 6 | 7·350 | 5·125 | 5·230 |
| Sulphur ..... | 16·03 | 8·380 | 7 | 8·575 | 1·870 | 1·913 |
| Platinium ..... | 98·84 | 5·563 | 4½ | 5·512 | 17·931 | 17·766 |
| Uranium..... | 217·26 | 25·790 | 21 | 25·725 | 8·445 | 8·425 |
| Magnesium..... | 12·69 | 5·665 | 4½ | 5·512 | 2·302 | 2·240 |

The results above tabulated are, we think, sufficient to render it evident that the specific volumes of the metals in a perfectly divided state are strict multiples of the volume 1·225.

### *Specific gravity of Melted Metals.*

We now sought an additional confirmation of our views in the volumes of metals in the melted state. And as no doubt could be entertained that this condition would completely obviate the influence of cohesion or that of any particular arrangement of particles, we felt that a complete confirmation

* The volumes of metals in this table are not always the same as those in Table I.; the reasons of the difference will be given in a future part of this memoir.

or refutation of all the views we have advanced would depend upon the results arrived at with the fused metals. The instrument we employed when the metals could be fused at a low temperature, consisted simply of a small glass matrass (see Figure), formed by blowing a bulb at one end of a tube of about a quarter of an inch diameter. The content of the bulb was ascertained by finding the weight of mercury which could fill it up to a given point of the stem, say *x*. A quantity of mercury equivalent in volume to five grains of water was then added, and another mark made at *y*. This done, the matrass was filled with small pieces of the metal under examination and carefully exposed to heat. As the metal melted, additional portions were introduced until the liquid metal stood somewhere between the marks *x* and *y*, the exact position being determined to within one-tenth of the space. The whole having then been allowed to cool, the matrass was broken and the metal weighed.




*Specific gravity of melted Lead.*

*Exp.* 1.—Capacity of matrass in grs. of water at 40° 124·17
Capacity corrected for expansion of glass 125·18
Weight of the lead . . . . . 1316grs.
Sp. gr. of the melted metal . . . . . 10·513

*Exp.* 2.—Capacity of the matrass . . . 64·37
Capacity corrected for expansion 64·90
Weight of the lead . . . . . 678·2 grains
Sp. gr. of melted metal . . . 10·45

*Exp.* 3.—Capacity of matrass . . . . 43·83
Capacity corrected for expansion 44·20
Weight of lead . . . . . 466·9 grains
Sp. gr. . . . . 10·563

| | | |
|---|---|---|
| I. | Sp. gr. of melted lead | 10·513 |
| II. | ... ... | 10·450 |
| III. | ... ... | 10·563 |
| | Mean . . | 10·509 |

*Specific gravity of melted Tin.*

*Exp.* 1.—Capacity of matrass . . 116·9
Corrected for expansion . 117·57
Weight of tin . . . . 817 grains
Sp. gr. . . . . 6·949

*Exp.* 2.—Capacity of matrass . . 151·52
Corrected for expansion . 152·38
Weight of tin . . . . 1053·5 grains
Sp. gr. . . . . 6·913

*Exp.* 3.—Capacity of matrass . . 133·38
Corrected for expansion . 134·15
Weight of tin . . . . 931 grains
Sp. gr. . . . . 6·94

I. Sp. gr. of melted tin 6·949
II. ... ... 6·913
III. ... ... 6·940
Mean . . 6·934

*Specific gravity of melted Bismuth.*

*Exp.* 1.—Capacity of matrass . . 98·65
Corrected for expansion . 99·28
Weight of bismuth . . 974 grains
Sp. gr. . . . . 9·811

*Exp.* 2.—Capacity of matrass . . 129·2
Corrected for expansion . 130
Weight of bismuth . 1268·3 grains
Sp. gr. . . . . 9·756

*Exp.* 3.—Capacity of matrass . . . . 141·88
Corrected for expansion of glass 142·78
Weight of bismuth . . . . 1414·3 grains
Sp. gr. . . . . 9·905

*Exp.* 4.—Capacity of matrass . . 103·52
Corrected for expansion . 104·20
Weight of bismuth . . 1013 grains
Sp. gr. . . . . 9·721

I. Sp. gr. of melted bismuth 9·811
II. ... ... 9·756
III. ... ... 9·905
IV. ... ... 9·721
Mean . . 9·798

*Specific gravity of melted Zinc.*

*Exp.* 1.—Capacity of matrass . . 45·8
Corrected for expansion . 46·26
Weight of zinc . . . . 301·7 grains
Sp. gr. . . . . 6·522

*Exp.* 2.—Capacity of matrass . . 55·37
Corrected for expansion . 55·92
Weight of zinc . . . . 364·1 grains
Sp. gr. . . . . 6·511

*Exp.* 3.—Capacity of matrass . . 61·84
Corrected for expansion . 62·45
Weight of zinc . . . . 406·2 grains
Sp. gr. . . . . 6·504

| | | |
|---|---|---|
| I. | Sp. gr. of melted zinc | 6·522 |
| II. | ... ... | 6·511 |
| III. | ... ... | 6·504 |
| | Mean . . | 6·512 |

*Specific gravity of melted Potassium.*

| | |
|---|---|
| Capacity of matrass . . | 95·68 |
| Corrected . . . . . | 95·76 |
| Weight of potassium . . | 80·7 grains |
| Sp. gr. . . . . | 0·8427 |

*Specific gravity of melted Phosphorus.*

| | |
|---|---|
| Corrected capacity of matrass | 96 |
| Weight of phosphorus . . | 167·3 grains |
| Sp. gr. . . . . | 1·744 |

*Specific gravity of melted Sulphur.*

| | | |
|---|---|---|
| *Exp.* 1.— | Capacity of matrass . . | 151·03 |
| | Corrected for expansion . | 151·40 |
| | Weight of sulphur . . . | 273·5 grains |
| | Sp. gr. . . . . | 1·806 |
| *Exp.* 2.— | Capacity of matrass . . | 127·84 |
| | Corrected for expansion . | 128·16 |
| | Weight of sulphur . . . | 232·7 grains |
| | Sp. gr. . . . . | 1·815 |
| *Exp.* 3.— | Capacity of matrass . . | 131·74 |
| | Corrected for expansion . | 132·07 |
| | Weight of sulphur . . . | 237·9 grains |
| | Sp. gr. . . . . | 1·801 |
| *Exp.* 4.— | Capacity of matrass . . | 117·53 |
| | Corrected for expansion . | 117·80 |
| | Weight of sulphur . . . | 213·2 grains |
| | Sp. gr. . . . . | 1·809 |
| *Exp.* 5.— | Capacity of matrass . . | 156·16 |
| | Corrected for expansion . | 156·55 |
| | Weight of sulphur . . . | 282·4 grains |
| | Sp. gr. . . . . | 1·804 |

| | | |
|---|---|---|
| I. | Sp. gr. of melted sulphur | 1·806 |
| II. | ... ... | 1·815 |
| III. | ... ... | 1·801 |
| IV. | ... ... | 1·809 |
| V. | ... ... | 1·804 |
| | Mean . . | 1·807 |

*Specific gravity of Sulphur in the viscid melted state.*

| | |
|---|---|
| Capacity of matrass . . | 156·03 |
| Corrected for expansion . | 156·50 |
| Weight of sulphur . . . | 273·5 grains |
| Sp. gr. . . . . | 1·748 |

*Specific gravity of melted Antimony.*—We found that the temperature at which this metal enters into fusion was too high for even German glass to bear without changing figure; consequently we had now to make a complete change in our manner of operating. We took two capsules of white earthenware, one of which was deep and narrow, the other wide and shallow. When capsule *b* was filled with melted metal, capsule *a* was placed upon its top, so that its convex surface pressed out part of the metal from capsule *b*. When all had cooled the weight of the metal was ascertained and compared with the weight of mercury capable of being held between the capsules. We have estimated the expansion of the capsules at $\frac{1}{600}$th of their bulk for 180°, which is the mean of the expansions of brown earthenware and stoneware as given by Dalton*.




| | | |
|---|---|---|
| *Exp.* 1.—Capacity between capsules . . | | 45·88 |
| Corrected for their expansion . | | 46·33 |
| Weight of antimony . . . . | | 308 grains |
| Sp. gr. . . . . | | 6·646 |
| *Exp.* 2.—Capacity between capsules . . | | 46·01 |
| Corrected for their expansion . | | 46·47 |
| Weight of antimony . . . . | | 303·4 grains |
| Sp. gr. . . . . | | 6·529 |
| I. Sp. gr. of melted antimony | | 6·646 |
| II. ... ... | | 6·529 |
| Mean . . | | 6·587 |

*Specific gravity of melted Copper.*

| | |
|---|---|
| Capacity between capsules . . | 49·97 |
| Corrected for their expansion . | 50·88 |
| Weight of copper . . . . . | 370 grains |
| Sp. gr. . . . . | 7·272 |

* New System of Chemistry, part 1. p. 44.

*Specific gravity of melted Silver.*

*Exp.* 1.—Capacity between capsules . . 55·61
Corrected for their expansion . 56·55
Weight of silver . . . . . 516·5 grains
Sp. gr. . . . . 9·131

*Exp.* 2.—Capacity between capsules . . 54·62
Corrected for their expansion . 55·54
Weight of silver . . . . . 515·5 grains
Sp. gr. . . . . 9·281

I. Sp. gr. of melted silver 9·131
II. ... ... 9·281
Mean . . 9·206

*Specific gravity of fluid Mercury.*—The density of this metal at 39°·2 is 13·588 according to Kupffer. Hence its specific gravity near the point of congelation will be 13·694.

TABLE IV.—Showing the Volumes of several Metals and other simple bodies after entering into Fusion.

| Designation. | | Volume. | | | | |
|---|---|---|---|---|---|---|
| Name. | Atomic weight. | Volume by experiment. | 1·225 as unity. | Volume by theory. | Sp. gr. by theory. | Sp. gr. by experiment. |
| Mercury | 101·43 | 7·407 | 6 | 7·350 | 13·800 | 13·694 |
| Tin | 58·92 | 8·497 | 7 | 8·575 | 6·871 | 6·934 |
| Bismuth | 71·07 | 7·254 | 6 | 7·350 | 9·670 | 9·798 |
| Lead | 103·73 | 9·871 | 8 | 9·800 | 10·584 | 10·509 |
| Zinc | 32·31 | 4·961 | 4 | 4·900 | 6·594 | 6·512 |
| Antimony | 64·62 | 9·810 | 8 | 9·800 | 6·594 | 6·587 |
| Silver | 108·30 | 11·764 | $9\frac{1}{2}$ | 11·637 | 9·306 | 9·206 |
| Copper | 31·65 | 4·352 | $3\frac{1}{2}$ | 4·287 | 7·383 | 7·272 |
| Potassium | 39·30 | 46·620 | 38 | 46·550 | 0·844 | 0·843 |
| Phosphorus | 31·44 | 18·028 | 15 | 18·375 | 1·711 | 1·744 |
| Sulphur | 16·03 | 8·871 | $7\frac{1}{4}$ | 8·881 | 1·805 | 1·807 |
| Viscid sulphur | 16·03 | 9·170 | $7\frac{1}{2}$ | 9·187 | 1·745 | 1·748 |

By inspecting the above table it will be seen that the atomic volumes of the metals are in general in a simple multiple ratio one to another, and are at the same time in a simple ratio with the volume of ice, and with the volume 11 given in our former paper. Perhaps the most curious and least expected results are those with copper and silver. These metals appear to assume in the melted state half a volume more than they possess in the solid state. This is highly interesting in the case of copper, as it explains the reason why CuO has a volume $3\frac{1}{2} + 2$ instead of $3 + 2$. We will not however in-

sist strongly upon this point until we shall have repeated the experiments with copper and silver more frequently, and with a more exact apparatus than we have hitherto been able to employ. The specific gravity of sulphur is also very interesting on account of the states into which it enters; of these we have examined five, viz.—

| | Sp. gr. | Volume. |
|---|---|---|
| Viscid melted state . . . . . | 1·748 | 9·170 |
| Clear amber melted . . . . . | 1·807 | 8·871 |
| Flowers . . . . . | 1·913 | 8·380 |
| Crystals . . . . . | 2·010 | 7·975 |
| Waxy by pouring the viscid sulphur into water . . . . . | 1·921 | 8·340 |

To the relations between the different states of this element we shall have to return.

Having now examined three of the conditions in which the metals present themselves, we shall conclude the section by recapitulating the principal points at which we think we have arrived.

1st. The metals, when obtained in a finely divided state, so as to be deprived of cohesion, exhibit volumes which are multiples of the unit 1·225.

2nd. The volumes of metals rendered fluid by heat are in like manner multiples of the volume 1·225.

3rd. The volumes of metals in the solid crystalline condition are, in general, multiples of a number about $\frac{1}{20}$th less than 1·225. We believe that this may *partly* arise from the peculiar molecular arrangement, but that the contraction is *principally* occasioned by the operation of the force of cohesion. Our first table, which gives volumes, as we have already observed, only approximating to multiples of 1·225, though serving to point out the existence of a law, would show a much greater coincidence between the theoretical and actual results than it does at present, if we were to apply a small correction to the observed volumes as we have done in Table II. In some instances of Table I. the volume is $\frac{1{\cdot}225}{2}$ less than it would have been after applying the empirical correction of $\frac{1}{20}$th. May we not therefore suppose that the contraction occasioned by cohesion is itself in some measure guided by the number 1·225? We think this is not improbable, but until we shall have given the subject a more minute investigation, it will be premature to insist strongly upon such a view.

We now proceed to test the law with a class of compounds which do not so readily yield to the solicitation of cohesion.

## Section II.

### *Oxides of the Metals.*

*Protoxide of Manganese*, MnO = 35·7.—The oxide examined was made by passing hydrogen over the hydrate of the protoxide while it was heated to redness. 18·83 grains of the oxide thus prepared gave an increase in the stem of the volumenometer of 3·5, making the sp. gr. 5·38 and the atomic volume 6·63.

*Sesquioxide of Manganese*, $Mn_2O_3$ = 79·4.—The oxide used in our experiments was prepared by calcining the nitrate. 24·53 grains gave an increase of 5·37 in one experiment and 5·31 in another.

I. Sp. gr. 4·568
II. ... 4·619

The mean result, 4·593, yields the volume 17·29. Our result does not differ widely from that obtained by Leonhard as the sp. gr. of Braunit, native sesquioxide, viz. 4·82.

*Manganoso-Manganic Oxide*, $Mn_2O_3 + MnO$ = 115·1.—This common oxide of manganese was obtained by calcining the pure carbonate in open air. 23·73 grains gave an increase in two experiments of 5·0 and 5·1 respectively.

I. Sp. gr. 4·746
II. ... 4·653

The mean, 4·700, gives the volume 24·49, a result almost identical with that obtained by Leonhard for hausmanite, viz. 4·72.

*Peroxide of Manganese*, $MnO_2$ = 43·7.—Turner has determined the sp. gr. of pyrolusite, native peroxide, and states it to be 4·81, which makes the atomic volume 9·09.

*Varvicite*, $2(MnO_2) + Mn_2O_3 + HO$ = 175·8.—According to Turner this mineral possesses sp. gr. 4·531, which gives 38·8 for the atomic volume.

*Peroxide of Iron*, $Fe_2O_3$ = 80·0.—The specific gravity of this oxide varies according to the temperature to which it has been exposed. Two specimens, heated short of redness, gave the following results: 24·70 gave an increase of 5·37, and the same quantity in the second experiment gave an increase of 5·19.

I. Sp. gr. 4·60
II. ... 4·759

The mean, 4·679, gives the atomic volume 17·09.

But the same oxide, raised by means of a wind lamp to a heat

approaching whiteness, gave a different result. 24·70 of the heated oxide gave an increase of only 4·81, making sp. gr. 5·135 and atomic vol. 15·57. Boullay has obviously examined the oxide in this last state, for he describes the sp. gr. as 5·225.

*Magnetic Oxide of Iron*, $Fe_2O_3 + FeO = 116$.—A specimen artificially prepared by Mercer's method of precipitating boiling solutions in atomic proportions of the sulphates of the protoxide and peroxide of iron, gave us a sp. gr. of 5·453. The native ore gives similar results. The recorded specific gravities of the magnetic oxide are as follow :—

| | |
|---|---|
| | 5·400 Boullay. |
| | 5·453 P. and J. |
| | 4·900 Leonhard. |
| | 5·200 Leonhard. |
| | 4·960 Gerolt. |
| | 5·094 Mohs. |
| Mean . . | 5·168 |

The mean, 5·168, gives the atomic volume 22·44.

*Protoxide of Cobalt*, $CoO = 37·5$.—19·87 grains gave an increase of 3·55, making the sp. gr. 5·597 and the atomic volume 6·70; the same oxide heated to whiteness possessed the sp. gr. 5·75 on operating on 30·13 grains.

*Peroxide of Cobalt*, $Co_2O_3 = 83$.—This oxide was prepared by heating the nitrate. 24·94 grains gave an increase of 5·18, making the sp. gr. 4·814 and the volume 17·24. Herapath describes an oxide of cobalt examined by him as having the sp. gr. 5·322, which would give a volume 15·6, and correspond to the strongly ignited peroxide of iron.

*Protoxide of Nickel*, $NiO = 37·5$.—39·74 grains increased 7·10, making sp. gr. 5·597, and atomic vol. 6·70. Genth describes the abnormal oxide of nickel discovered by him as having a sp. gr. of 5·745.

*Peroxide of Nickel*, $Ni_2O_3 = 83·0$.—The oxide used in our experiments was prepared by calcining the nitrate. 27·33 grains gave an increase of 5·68, making the sp. gr. 4·814, and atomic vol. 17·24, a result closely agreeing with that obtained by Herapath, who found the sp. gr. 4·846, and the consequent vol. 17·12. The mean gives 4·830 as the sp. gr., and 17·18 as the atomic vol.

*Oxide of Zinc*, $ZnO = 40·3$.—Boullay describes the sp. gr. as 5·60; Karsten as 5·734; and Mohs as 5·432. The mean sp. gr., 5·588, gives the atomic volume 7·21.

*Suboxide of Copper*, $Cu_2O = 71·20$.—This oxide was prepared according to Bottger's plan, by boiling a solution of oxide

of copper in sugar and potash, and was obtained of a beautiful red colour. 20·8 grains gave the increase 3·62, making sp. gr. 5·746. The result obtained by Karsten with the native suboxide, 5·751, and that of Leroyer and Dumas, 5·75, agree closely with our determination. The mean sp. gr., 5·749, gives 12·38 as the atomic volume.

*Protoxide of Copper*, CuO = 39·60.—This oxide was prepared by igniting the nitrate, avoiding too high a temperature. 22·12 grains gave an increase of 3·75, making sp. gr. 5·90 and atomic volume 6·71. Boullay found the sp. gr. to be 6·13; Karsten 6·430; and Herapath 6·401. To ascertain whether the difference of results was due to contraction at a high temperature, a portion of the same oxide was exposed to a white heat; 26·62 grains now gave an increase of 4·15, making the sp. gr. 6·414 and the atomic volume 6·17.

*Oxide of Cadmium*, CdO = 63·80.—Karsten states the specific gravity of this oxide at 6·950, which gives 9·18 for the atomic volume.

*Oxide of Chromium*, $Cr_2O_3$ = 80·0.—The oxide of chromium occurs in two distinct states, commonly known as the brown and green oxides.

The green oxide gave the following result:—24·3 grains gave an increase of 4·95, making sp. gr. 4·909. Wöhler found the sp. gr. of the crystallized oxide 5·210. The mean gives sp. gr. 5·059, and atomic volume 15·81.

*Oxide of Bismuth*, BiO = 79·07.—26·5 grains of this oxide gave an increase of 3·28, making the sp. gr. 8·079 and the atomic volume 9·79. Karsten found a sp. gr. of 8·173.

*Oxide of Tin*, SnO = 65·90.—According to Herapath, the specific gravity of this oxide is 6·666, its atomic volume will therefore be 9·8.

*Peroxide of Tin*, $SnO_2$ = 73·9.—Herapath describes the specific gravity of this oxide as 6·640; hence its atomic volume will be 11·1.

*Arsenious Acid*, $AsO_3$ = 99·34.—This acid has been frequently examined, and the following results are those possessing the greatest uniformity:—

3·702 Karsten.
3·695 Guibourt.
3·690 Leonhard.
3·710 Leonhard.
3·698 Royer and Dumas.

The mean, sp. gr. 3·699 yields 26·86 as the atomic volume.

*Arsenic Acid*, $AsO_5$ = 115·34.—29·53 grains gave in one experiment an increase of 7·34, in another of 7·41, making

the sp. gr. respectively 4·023 and 3·985. Karsten states it at 3·734. The mean, 3·914, gives the atomic volume 29·47.

*Oxide of Antimony*, $SbO_3 = 153·28$.—26·52 grains of this oxide caused an increase of 5·05, making a sp. gr. of 5·251 and a volume of 29·19.

*Antimonious Acid*, $SbO_4 = 161·28$.—20·37 grains of this compound, prepared by igniting antimonic acid, gave an increase of 5·0, making the sp. gr. 4·074, and atomic volume 39·59.

*Antimonic Acid*, $SbO_5 = 169·28$.—This acid, prepared in the usual way by treating the oxide with nitric acid, and gently igniting the residue, gave the specific gravity 3·779, and atomic volume 45·06.

*Oxide of Molybdenum*, $MoO_2 = 63·96$.—According to Bucholz, this oxide has a sp. gr. of 5·666, which gives the atomic volume 11·28.

*Molybdic Acid*, $MoO_3 = 71·96$.—According to Berzelius, the sp. gr. of this acid is 3·49; according to Thomson 3·46. The mean, 3·475, gives the atomic volume 20·71.

*Tungstic Oxide*, $WO_2 = 110·8$.—According to Karsten, this oxide has a sp. gr. 12·11; hence its atomic volume will be 9·14.

*Tungstic Acid*, $WO_3 = 118·8$.—It is well known that this acid heightens in colour as the heat to which it has been exposed is increased. The specific gravity probably differs in the same proportion, and this may account for the contradictory results given by chemists with respect to its specific gravity. De Luyart states it at 6·12; Herapath at 5·274; and Karsten at 7·139. The mean result, 6·177, gives the atomic volume as 19·23.

*Titanic Acid*, $TiO_2 = 40·33$.—Titanic acid occurs in various forms, to which especial reference will afterwards be made. In the meantime we assume Brookite as the representative of this oxide. The sp. gr. of that mineral, 4·128, gives 9·77 as the atomic volume.

*Uranous Oxide*, $UO = 68$.—According to Richter, this oxide has a sp. gr. of 6·94, making the atomic vol. 9·8.

*Hydrated Uranic Oxide*, $U_2O_3 + HO = 153$.—Gmelin describes this oxide as having a sp. gr. of 5·926, making an atomic volume of 25·82.

*Uranoso-Uranic Oxide*, $UO + U_2O_3 = 212$.—Karsten states that this oxide enjoys the sp. gr. 7·193, making the atomic volume 29·47.

*Suboxide of Lead*, $Pb_2O = 215·2$.—This oxide was made by slowly heating the oxalate to redness. 48·47 grains gave increase 4·96, making sp. gr. 9·772, and atomic vol. 22·02.

*Protoxide of Lead*, PbO = 111·6.—48·47 grains gave an increase of 5·24, making sp. gr. 9·250. Herapath states it at 9·277; Karsten at 9·209. The mean result, 9·245, gives the volume 12·07.

*Peroxide of Lead*, $PbO_2$ = 119·6.—The oxide experimented upon was made by projecting the protoxide into melted chlorate of potash. 41·46 grains gave an increase of 4·66, making sp. gr. 8·897; in a second experiment 32·3 grains gave increase 3·69, making sp. gr. 8·756. Herapath states the sp. gr. at 8·90. The mean of the three results is 8·851, making the atomic vol. 13·51.

*Minium*, $PbO_2 + 2PbO$ = 342·8.—Herapath describes the specific gravity of this compound as 9·096; its atomic volume must therefore be 37·7. Boullay states the sp. gr. at 9·190, a result confirmatory of Herapath's experiment.

*Suboxide of Mercury*, $Hg_2O$ = 210·8.—Herapath describes the density of this oxide as 10·69, which gives a volume of 19·70.

*Protoxide of Mercury*, HgO = 109·8.—56·72 grains of this oxide, prepared from the nitrate, gave an increase of 5·0, making the sp. gr. 11·344. Berzelius found the sp. gr. 11·074; Herapath 11·085; Karsten 11·196; Boullay 11·000; and Le Royer and Dumas 11·29. The mean sp. gr., 11·164, gives the atomic volume 9·83.

*Oxide of Silver*, AgO = 116·0.—Boullay describes the sp. gr. of this oxide as 7·250; Herapath as 7·140; and we ourselves found it 7·147 in an experiment with 44·10 grains. The mean of these results, 7·179, gives the atomic volume 16·14.

*Potash*, KO = 47·15.—According to Karsten, anhydrous potash has a sp. gr. 2·656; its atomic volume is therefore 17·75.

*Soda*, NaO = 31·3.—Karsten describes the sp. gr. of anhydrous soda as 2·805; hence its atomic volume is 11·1.

*Barytes*, BaO = 76·70.—23·86 grains of anhydrous barytes gave an increase of 4·94, and in another experiment 4·785, giving the specific gravity 4·829 and 4·986 respectively. Karsten states it at 4·733. The mean, 4·849, gives an atomic volume 15·82.

*Peroxide of Barium*, $BaO_2$ = 84·70.—23·86 grains of this oxide, made by passing an excess of oxygen over barytes heated in a porcelain tube, gave the increase 4·812, making the sp. gr. 4·958, and atomic volume 17·08.

*Strontia*, SrO = 51·80.—Karsten states the specific gravity of anhydrous strontia at 3·932; hence its atomic volume will be 13·2.

## TABLE V.—Showing the Atomic Volumes and Specific Gravities of the Metallic Oxides.

| Designation. | | Specific gravity and atomic volume. | | | | | |
|---|---|---|---|---|---|---|---|
| Name. | Formula. | Atomic weight. | Volume by experiment. | 1·925 taken as a standard for comparison. | Volume by theory. | Specific gravity by experiment. | Specific gravity by theory. |
| Protoxide of manganese ... | $MnO$ | 35·7 | 6·63 | $5\frac{1}{2}$ | 6·73 | 5·380 | 5·304 |
| Sesquioxide of manganese... | $Mn_2O_3$ | 79·4 | 17·29 | 14 | 17·15 | 4·593 | 4·629 |
| Red oxide of manganese ... | $MnO + Mn_2O_3$ | 115·1 | 24·49 | 20 | 24·5 | 4·700 | 4·697 |
| Peroxide of manganese ..... | $MnO_2$ | 43·7 | 9·09 | $7\frac{1}{2}$ | 9·18 | 4·810 | 4·760 |
| Varvicite ..... | $\{2(MnO_2)+(Mn_2O_3) + HO\}$ | 175·8 | 38·8 | 32 | 39·20 | 4·531 | 4·484 |
| Peroxide of iron..... | $Fe_2O_3$ | 80·0 | 17·09 | 14 | 17·15 | 4·679 | 4·664 |
| ——— strongly heated . | $Fe_2O_3$ | 80·0 | 15·57 | 13 | 15·93 | 5·135 | 5·031 |
| Magnetic oxide of iron ..... | $FeO + Fe_2O_3$ | 116·0 | 22·44 | 18 | 22·05 | 5·168 | 5·260 |
| Oxide of cobalt ..... | $CoO$ | 37·5 | 6·70 | $5\frac{1}{2}$ | 6·73 | 5·597 | 5·572 |
| Peroxide of cobalt ..... | $Co_2O_3$ | 83·0 | 17·24 | 14 | 17·15 | 4·814 | 4·830 |
| ——— strongly heated?. | $Co_2O_3$ | 83·0 | 15·6 | 13 | 15·93 | 5·322 | 5·220 |
| Oxide of nickel ..... | $NiO$ | 37·5 | 6·70 | $5\frac{1}{2}$ | 6·73 | 5·597 | 5·572 |
| Peroxide of nickel ..... | $Ni_2O_3$ | 83·0 | 17·18 | 14 | 17·15 | 4·830 | 4·839 |
| Oxide of zinc ..... | $ZnO$ | 40·3 | 7·21 | 6 | 7·35 | 5·588 | 5·482 |
| Suboxide of copper ..... | $Cu_2O$ | 71·20 | 12·38 | 10 | 12·25 | 5·749 | 5·812 |
| Oxide of copper..... | $CuO$ | 39·6 | 6·71 | $5\frac{1}{2}$ | 6·73 | 5·90 | 5·884 |
| ——— strongly heated . | $CuO$ | 39·6 | 6·17 | 5 | 6·12 | 6·414 | 6·470 |
| Oxide of cadmium..... | $CdO$ | 63·8 | 9·18 | $7\frac{1}{2}$ | 9·18 | 6·950 | 6·950 |
| Water (ice) ..... | $HO$ | 9·0 | 9·8 | 8 | 9·8 | 0·918 | 0·918 |
| Oxide of chromium strongly heated..... | $Cr_2O_3$ | 80·0 | 15·81 | 13 | 15·93 | 5·059 | 5·031 |
| Oxide of bismuth ..... | $BiO$ | 79·07 | 9·79 | 8 | 9·8 | 8·079 | 8·068 |
| Oxide of tin ..... | $SnO$ | 65·9 | 9·8 | 8 | 9·8 | 6·666 | 6·666 |
| Peroxide of tin ..... | $SnO_2$ | 73·9 | 11·1 | 9 | 11·02 | 6·640 | 6·705 |
| Arsenious acid ..... | $AsO_3$ | 99·34 | 26·86 | 22 | 26·95 | 3·699 | 3·680 |
| Arsenic acid ..... | $AsO_5$ | 115·34 | 29·47 | 24 | 29·40 | 3·914 | 3·923 |
| Oxide of antimony..... | $SbO_3$ | 153·28 | 29·19 | 24 | 29·40 | 5·251 | 5·213 |
| Antimonious acid ..... | $SbO_4$ | 161·28 | 39·59 | 32 | 39 2 | 4·074 | 4·114 |
| Antimonic acid ..... | $SbO_5$ | 169·28 | 45·06 | 36 | 44·1 | 3·779 | 3·838 |
| Molybdic oxide ..... | $MoO_2$ | 63·96 | 11·28 | 9 | 11·02 | 5·666 | 5·803 |
| Molybdic acid ..... | $MoO_3$ | 71·96 | 20·71 | 17 | 20·82 | 3·475 | 3·456 |
| Tungstic oxide ..... | $WO_2$ | 110·8 | 9·14 | $7\frac{1}{2}$ | 9·18 | 12·11 | 12·070 |
| Tungstic acid ..... | $WO_3$ | 118·8 | 19·23 | 16 | 19·60 | 6·177 | 6·061 |
| Titanic acid (brookite) ..... | $TiO_2$ | 40·33 | 9·77 | 8 | 9·80 | 4·128 | 4·115 |
| Uranous oxide ..... | $UO$ | 68 | 9 8 | 8 | 9 8 | 6·94 | 6·938 |
| Hydrated uranic oxide ..... | $U_2O_3 + HO$ | 153 | 25·82 | 21 | 25·72 | 5·926 | 5·971 |
| Uranoso-uranic oxide ..... | $UO + U_2O_3$ | 212 | 29·47 | 24 | 29·4 | 7·193 | 7·210 |
| Suboxide of lead ..... | $Pb_2O$ | 215·2 | 22·02 | 18 | 22·05 | 9·772 | 9·759 |
| Protoxide of lead ..... | $PbO$ | 111·6 | 12·07 | 10 | 12·25 | 9·245 | 9·110 |
| Peroxide of lead..... | $PbO_2$ | 119·6 | 13·51 | 11 | 13·47 | 8·851 | 8·878 |
| Minium ..... | $PbO_2 + 2\ Pbo$ | 342·8 | 37·7 | 31 | 37·97 | 9·096 | 9·028 |
| Suboxide of mercury..... | $Hg_2O$ | 210·8 | 19·70 | 16 | 19·6 | 10·69 | 10·755 |
| Peroxide of mercury ..... | $HgO$ | 109·8 | 9·83 | 8 | 9·8 | 11·164 | 11·204 |
| Oxide of silver ..... | $AgO$ | 116·0 | 16·14 | 13 | 15·9 | 7·179 | 7·295 |
| Potash ..... | $KO$ | 47·15 | 17·75 | 14 | 17·15 | 2·656 | 2·749 |
| Soda ..... | $NaO$ | 31·3 | 11·10 | 9 | 11·02 | 2·805 | 2·813 |
| Barytes ..... | $BaO$ | 76·70 | 15·82 | 13 | 15·90 | 4·849 | 4·824 |
| Peroxide of barium ..... | $BaO_2$ | 84·70 | 17·08 | 14 | 17·15 | 4·958 | 4·938 |
| Strontia ..... | $SrO$ | 51·80 | 13·20 | 11 | 13·47 | 3·932 | 3·845 |
| Magnesia ..... | $MgO$ | 20·7 | 6·60 | $5\frac{1}{2}$ | 6·73 | 3·135 | 3·075 |
| Lime ..... | $CaO$ | 28·5 | 9·13 | $7\frac{1}{2}$ | 9·18 | 3·12 | 3·104 |

*Magnesia*, MgO = 20·7.—Richter states the sp. gr. of this earth at 3·07; Karsten at 3·20. The mean, 3·135, gives 6·60 as the atomic volume.

*Lime*, CaO = 28·5.—Royer and Dumas describe the sp. gr. of anhydrous lime as 3·08; Karsten states it at 3·16. The mean gives 3·12 as the sp. gr., 9·13 as the atomic vol.

In the preceding list of metallic oxides, we have given the specific gravity of all those the composition of which has been well-ascertained. By tabulating the results we have decisive proof that the number 1·225 or $\frac{1\cdot225}{2}$ is the primitive volume of the metallic oxides.

There can no longer, therefore, be a doubt that either 1·252 or $\frac{1\cdot225}{2}$ forms the sub-multiple for this large class of compounds. But it is not this fact, in its general enunciation, that is the principal point of interest in the table, for we learn from it at the same time, that, in most of the oxides, 1·225 × 2 forms the combining volume of oxygen. In the class of magnesian metals we find sometimes the volume $\frac{1\cdot225}{2}$, but only when the oxide has not been strongly heated. Are we then to adopt ·6125 as the standard volume? We still prefer using for the present 1·225 as the standard for comparison, especially as we conceive that the equivalents of the magnesian metals should be doubled. We know various hydrates of the magnesian oxides and of their salts, in which *two* equivalents of the oxide or salt combine with *one* equivalent of water. Instances of this are found in hydrated peroxide of manganese, and in Johnston's sulphate of lime. We know also that we require to use *two* equivalents of a magnesian oxide to substitute *one* of an oxide of the potash family. From these reasons alone we have almost the right to demand an increase in the equivalents of the magnesian metals. But add to this the simplicity which would ensue were this done, and our right to demand the increase becomes much greater. This class of metals favours us with the following series of oxides:—

$$R_2O - RO - R_2O_3 - RO_2.$$

But the above series, besides being unnaturally complex, is not complete, as it wants the element $R_3O_2$. It would therefore be more rational as well as more simple, to double the equivalents of the magnesian metals, in which case the series would be one of arithmetical progression:

$$RO - RO_2 - RO_3 - RO_4.$$

Admitting this view, the division of 1·225 ceases to be necessary.

At present we cannot discuss with propriety the difference of volumes of an oxide before and after being heated, but we are prepared to give a satisfactory account of this difference in the latter part of the paper. We must content ourselves at present with pointing out the general facts exhibited by the table under consideration.

In the first place, we are shown by it, that, in general, the oxygen in the oxides possesses the volume $1{\cdot}225 \times 2$. Thus the protoxides of the magnesian metals in their densest state possess the volume $1{\cdot}225 \times 5$. We have already seen that the magnesian radical has a vol. $1{\cdot}225 \times 3$; hence oxygen in the protoxides enjoys two unit volumes. Representing 1·225 by v, the following rule prevails for the protoxide:—

$$RO, v \times 5 = R, v \times 3 + O, v + 2.$$

The same rule holds generally for all protoxides having the formula RO, the value of the oxide being the corresponding Rv added to $Ov \times 2$, cadmium and tin being exceptions, although in all probability CdO would cease to be an exception, if that oxide were examined after strong ignition. The Rv must in all cases be taken in the state when it exhibits itself in its natural power uncontrolled by cohesion. The exception of StO, in which O is made to possess a unit vol., is obviously connected with the dimorphous relations of the metal. But although O, in the oxides RO, generally possesses two unit volumes, it does not do so in all the oxides: thus the second equivalent O in $BaO_2$, $SnO_2$, $PbO_2$ possesses only one unit volume. In the case of $Cu_2O$, $Ni_2O_3$, $Mn_2O_3$ &c., it is highly probable that the metal assumes a volume of $v \times 4$ as in zinc. If so, the O in these compounds will still enjoy a volume of $v \times 2$. Again, if, in the case of ice, we assume the volume of the O to be $v \times 2$, the volume of H will be $v \times 6$, which would exactly coincide with the volumes of the other magnesian metals, if, according to what we have already said, their equivalents were doubled. There are other points of interest in the Table, the consideration of which we defer to another place.

## Section III.

### *Sulphurets.*

*Sulphuret of Manganese*, MnS = 43·8.—The following estimations are given of manganese-glance:—

| | |
|---|---|
| 3·95 | Leonhard. |
| 4·01 | Leonhard. |
| 4·014 | Mohs. |
| Mean . . | 3·991 |

This makes the atomic volume 10·98.

*Subsulphuret of Iron*, $Fe_2S = 72·1$.—This sulphuret was made by passing hydrogen over FeO, $SO_3$ at a red heat. 19·2 grains gave an increase of 3·31; hence the sp. gr. is 5·80, and the atomic volume 12·43.

*Sulphuret of Iron*, $FeS = 44·1$.—A specimen made by holding sulphur in contact with iron at a white heat, yielded the following result:—38·3 grains gave an increase of 7·59, making sp. gr. 5·046. Another specimen, prepared by fusing iron with sulphur, was examined in like manner. 38·3 grains gave an increase of 7·62, making sp. gr. 5·026. The mean result, 5·035, gives an atomic volume 8·75.

*Sesquisulphuret of Iron*, $Fe_2S_3 = 104·3$.—This sulphuret was made by passing HS over $Fe_2O_3$ with the usual precautions. 15·16 grains gave an increase in one experiment of 3·62, in another 3·53. The mean, 3·57, gives the sp. gr. 4·246, and atomic volume 24·56.

*Bisulphuret of Iron*, $FeS_2 = 60·2$.—Karsten describes the sp. gr. of this compound as 4·90, from which we deduce the volume 12·28.

*Subsulphuret of Copper*, $Cu_2S = 79·3$.—Mohs describes the sp. gr. of copper-glance at 5·695, which makes the atomic volume 13·93.

*Sulphuret of Copper*, $CuS = 47·7$.—Walchner states the sp. gr. of this sulphuret at 3·8; Karsten at 4·163; the mean gives sp. gr. 3·981, and atomic volume 11·98.

*Sulphuret of Zinc*, $ZnS = 48·3$.—Karsten has determined the sp. gr. of this sulphuret at 3·923, which gives 12·3 for the atomic volume.

*Subsulphuret of Nickel*, $Ni_2S = 74·1$.—This sulphuret was made by passing H over NiO, $SO_3$ at a red heat. 12·1 grains gave an increase of 2·0, making sp. gr. 6·05, and atomic volume 12·24.

*Bisulphuret of Cobalt*, $CoS_2 = 61·7$.—This sulphuret made by heating the oxide of cobalt with an excess of sulphur gave the following results. 22·8 grains gave increase 5·31 in one experiment, and 5·37 in another; the mean, 5·34, gives sp. gr. 4·269, and atomic volume 14·45.

*Sesquisulphuret of Chromium*, $Cr_2S_3 = 104$.—This sulphuret was made by passing dry HS over $Cr_2O_3$ at an elevated

temperature. 16·37 grains gave increase 4·0, making sp. gr. 4·092 and volume 25·41.

*Sulphuret of Bismuth*, BiS = 87·07.—According to Wehrle the sp. gr. is 7·807; to Herapath 7·591; to Karsten 7·000. The mean, 7·466, gives the atomic volume 11·66.

*Sulphuret of Cadmium*, CdS = 71·8—The sp. gr. of Greinocket was found by Breithaupt to be 4·90; its atomic volume is therefore 14·65.

*Sulphuret of Lead*, PbS = 119·7.—Karsten found its sp. gr. 7·50; Mohs 7·568; Leonhard 7·40 and 7·60; Brisson 7·587; and Musschenbroek 7·220. The mean, 7·479, gives the atomic volume 16·00.

*Sesquisulphuret of Lead*, $Pb_2S_3$ = 255·4.—This sulphuret was prepared by passing HS over $Pb_2O_3$ heated in the water-bath, the oxide being prepared as recommended by Winkelblech, by pouring chloride of soda into a solution of oxide of lead in potash. No separation of sulphur took place in the preparation. 16·6 grains gave increase 2·62, giving the sp. gr. 6·335, and atomic volume 40·32.

*Sulphuret of Platinum*, PtS = 114·9.—Bottger describes the sp. gr. of this sulphuret as 8·84, making the atomic volume 12·88.

*Bisulphuret of Platinum*, $PtS_2$ = 131·0.—Bottger's determination of 7·224 for the sp. gr. gives a volume of 18·1.

*Sulphuret of Silver*, AgS = 124.—Karsten's sp. gr. of 6·85 gives the volume 18·1.

*Sulphuret of Tin*, SnS = 74·3.—Boullay states the sp. gr. at 5·267; Karsten at 4·852. The mean, 5·059, gives a volume 14·67.

*Bisulphuret of Tin*, $SnS_2$ = 90·0.—According to Boullay, the sp. gr. is 4·415; according to Karsten 4·600. The mean, 4·507, gives an atomic volume of 19·97.

*Sulphuret of Molybdenum*, MoS = 64.—According to Mohs, the sp. gr. of this mineral is 4·59, which gives an atomic volume of 13·9.

*Sulphuret of Arsenic*, $As_2S_3$ = 123·7.—This compound has, according to Karsten, a sp. gr. of 3·459, making the atomic volume 35·7.

*Sulphuret of Antimony*, $Sb_2S_3$ = 177·5.—According to Mohs, this substance possesses the sp. gr. 4·62, and hence the volume must be 38·4.

TABLE VI.—Showing the Volumes of certain Sulphurets.

| Designation. | | | Volumes. | | | | |
|---|---|---|---|---|---|---|---|
| Name. | Formula. | Atomic weight. | Volume by experiment. | No. of 1·225 vols. | Volume by theory. | Specific gravity by experiment. | Specific gravity by theory. |
| Sulphuret of manganese | $MnS$ | 43·8 | 10·98 | 9 | 11·02 | 3·991 | 3·974 |
| Subsulphuret of iron | $Fe_2S$ | 72·1 | 12·43 | 10 | 12·25 | 5·80 | 5·885 |
| Sulphuret of iron | $FeS$ | 44·1 | 8·75 | 7 | 8·57 | 5·035 | 5·145 |
| Sesquisulphuret of iron | $Fe_2S_3$ | 104·3 | 24·56 | 20 | 24·50 | 4·246 | 4·257 |
| Bisulphuret of iron | $FeS_2$ | 60·2 | 12·28 | 10 | 12·25 | 4·90 | 4·914 |
| Subsulphuret of copper | $Cu_2S$ | 79·3 | 13·93 | 11 | 13·47 | 5·695 | 5·887 |
| Sulphuret of copper | $CuS$ | 47·7 | 11·98 | 10 | 12·25 | 3·981 | 3·894 |
| Sulphuret of zinc | $ZnS$ | 48·3 | 12·3 | 10 | 12·25 | 3·923 | 3·943 |
| Subsulphuret of nickel | $Ni_2S$ | 74·10 | 12·24 | 10 | 12·25 | 6·05 | 6·050 |
| Bisulphuret of cobalt | $CoS_2$ | 61·7 | 14·45 | 12 | 14·70 | 4·269 | 4·197 |
| Sesquisulphuret of chromium | $Cr_2S_3$ | 104 | 25·41 | 21 | 25·72 | 4·092 | 4·044 |
| Sulphuret of bismuth | $BiS$ | 87·07 | 11·66 | 9½ | 11·63 | 7·466 | 7·485 |
| Sulphuret of cadmium | $CdS$ | 71·8 | 14·65 | 12 | 14·70 | 4·90 | 4·884 |
| Sulphuret of lead | $PbS$ | 119·7 | 16·0 | 13 | 15·92 | 7·479 | 7·519 |
| Sesquisulphuret of lead | $Pb_2S_3$ | 255·4 | 40·31 | 33 | 40·42 | 6·335 | 6·318 |
| Sulphuret of platinum | $PtS$ | 114·9 | 12·9 | 11 | 13·47 | 8·84 | 8·530 |
| Bisulphuret of platinum | $PtS_2$ | 131 | 18·1 | 15 | 18·37 | 7·224 | 7·131 |
| Sulphuret of silver | $AgS$ | 124 | 18·1 | 15 | 18·37 | 6·85 | 6·750 |
| Sulphuret of tin | $SnS$. | 74·30 | 14·67 | 12 | 14·7 | 5·059 | 5·054 |
| Bisulphuret of tin | $SnS_2$ | 90·0 | 19·97 | 16 | 19·60 | 4·507 | 4·597 |
| Sulphuret of molybdenum | $MoS$ | 64 | 13·9 | 11½ | 14·08 | 4·59 | 4·545 |
| Sulphuret of arsenic | $AsS_3$ | 123·7 | 35·7 | 29 | 35·52 | 3·459 | 3·482 |
| Sulphuret of antimony | $SbS_3$ | 177·5 | 38·4 | 31 | 37·97 | 4·62 | 4·674 |

The above Table, besides affording additional evidence of the law of multiple proportions, embraces other points of interest to which we may briefly refer. We have already stated the volume of sulphur to be 7v. Testing therefore the results of the Table by the hypothesis of the sulphur retaining that volume in its combinations, we find—

1st. A class of sulphurets in which the volumes of both metal and sulphur remain the same as they are in the uncombined state. The following examples of this class are furnished by the Table:—

Sulphuret of copper . . Cu, 3v + S, 7v = CuS, 10v
Sulphuret of cadmium . Cd, 5v + S, 7v = CdS, 12v
Sulphuret of platinum . Pt, 4v + S, 7v = PtS, 11v
Sulphuret of molybdenum Mo, $4\frac{1}{2}$v + S, 7v = MoS, $11\frac{1}{2}$v.

2nd. A class in which the volumes of one or more of the atoms of metal or sulphur disappear, whilst the remaining atoms continue to possess the same volumes as when uncom-

bined. Of this very remarkable class we have several examples, viz.—

Subsulphuret of iron, Fe, 3v + Fe, 0v + S, 7v = $Fe_2S$, 10v
Sulphuret of iron, Fe, 0v + S, 7v = FeS, 7v
Sesquisulphuret of iron, $Fe_2$, 6v + S, 0v + $S_2$, 14v = $Fe_2S_3$, 20v
Bisulphuret of iron, Fe, 3v + S, 0v + S, 7v = $FeS_2$, 10v
Magnetic iron pyrites, $Fe_7$, 0v + $S_8$, 56v = $Fe_7S_8$, 56v
Subsulphuret of nickel, Ni, 3v + Ni, 0v + S, 7v = $Ni_2S$, 10v
Sesquisulphuret of chromium, $Cr_2$, 0v + $S_3$, 21v = $Cr_2S_3$, 12v

3rd. A class in which the sulphur assumes the volume 6v. In this group we have included the bisulphuret of cobalt in which the volume of the metal is merged.

Sulphuret of manganese Mn, 3v + S, 6v = MnS, 9v
Sulphuret of zinc . . Zn, 4v + S, 6v = ZnS, 10v
Sulphuret of silver . . Ag, 9v + S, 6v = AgS, 15v
Bisulphuret of cobalt . Co, 0v + $S_2$, 12v = $CoS_2$, 12v

There are several compounds included in the Table which do not come under the above heads, and the uncertainty whether their observed volumes are owing to the reduction in the volume of the metal or in that of the sulphur, prevents us from advancing anything very positive respecting them. There are however two substances, viz. the sulphuret and the sesquisulphuret of lead, in which Pb evidently assumes a volume of 6v: thus—

Pb, 6v + S, 7v = PbS, 13v
$Pb_2$, 12v + $S_3$, 21v = $Pb_2S_3$, 33v.

## Section IV.

### *Non-metallic Elements and their Oxides, and the Oxides of Metals of unknown specific gravity.*

*Sulphur and Carbon.*—For convenience these elements will be discussed in the following section:—

*Selenium*, Se = 39·60.—According to Berzelius, the sp. gr. varies from 4·30 to 4·32; Boullay found it exactly the mean, 4·31, which therefore we adopt as the specific gravity. This makes the atomic volume 9·188.

*Phosphorus*, P = 31·44.—The specific gravity of phosphorus is 1·77 according to Berzelius; this gives the atomic volume 17·76.

*Boron*, B = 10·9.—The sp. gr. of this element is generally

stated as twice that of water, in which case its volume = 5·45.

*Iodine*, I = 126·39.—Gay-Lussac and Thenard describe the sp. gr. of this element as 4·948, in which case its atomic volume is 25·54.

Taking 2·0 as the sp. gr. of charcoal, and 2·010 as that for crystallized sulphur, for reasons afterwards to be stated, we have the following table of non-metallic elements.

TABLE VII.—Showing the Volumes of certain Non-metallic Elements.

| | Atomic weight. | Volume by experiment. | 1·225 as standard. | Volume by theory. | Specific gravity by experiment. | Specific gravity by theory. |
|---|---|---|---|---|---|---|
| Carbon ..... | 12·00 | 6·00 | 5 | 6·12 | 2·0 | 1·96 |
| Sulphur ..... | 16·03 | 7·97 | 6½ | 7·96 | 2·010 | 2·013 |
| Selenium ..... | 39·60 | 9·188 | 7½ | 9·187 | 4·31 | 4·31 |
| Phosphorus ... | 31·44 | 17·76 | 14½ | 17·76 | 1·77 | 1·770 |
| Boron ..... | 10·90 | 5·45 | 4½ | 5·51 | 2·00 | 1·978 |
| Iodine..... | 126·39 | 25·54 | 21 | 25·72 | 4·948 | 4·914 |

In the above Table we have given the volumes of the elements without the reference to the power of cohesion which we made in a former part of the paper. But nevertheless the coincidence between the theoretical and experimental specific gravities is such that we are forced to admit either that the non-metallic elements are entirely free from the influence of cohesion, or that, as we have before hinted, the contraction thus occasioned exhibits itself in submultiples of the volume 1·225.

We have now to examine the volumes of certain oxides which were neglected in the previous sections, because we were ignorant of the specific gravity of their radicals.

*Boracic Acid*, $BO_3$ = 34·9.—The following estimations are given of the sp. gr. of vitreous boracic acid:—1·83 Berzelius, 1·803 Davy, 1·75 Breithaupt. Mean, 1·794, which gives the atomic volume 19·45.

*Phosphoric Acid*, $PO_5$ = 71·44.—This acid, in its vitreous state, has, according to Brisson, 2·387 sp. gr., and 29·74 atomic volume.

*Silica*, $SiO_3$ = 46·22.—Quartz has a sp. gr. of 2·66, according to the mean of many determinations. This gives the volume 17·37.

*Alumina*, $Al_2O_3$ = 51·4.—The ruby and sapphire possess sp. gr. 3·531, equal to an atomic volume of 14·56.

*Oxide of Thorium*, ThO = 67·6.—The sp. gr. of this oxide

is 9·402 according to Berzelius; hence its atomic volume will be 7·19.

*Glucina*, $G_2O_3 = 77$.—The sp. gr. of this earth is stated to be 3·0, in which case its volume is 25·66.

*Yttria*, $YO = 40·2$.—Ekeberg found the sp. gr. of this earth 4·842, which gives the volume 8·3.

*Zirconia*, $Zr_2O_3 = 91·4$.—This earth, according to Klaproth, has a sp. gr. 4·3, which is equivalent to an atomic volume of 21·2.

It must be borne in mind that considerable uncertainty exists with regard to the atomic weights of the last four bodies.

TABLE VIII.—Showing the Volume of Oxides of Elements of unknown specific gravity.

| Designation. | | | Volumes. | | | | |
|---|---|---|---|---|---|---|---|
| Name. | Formula. | Atomic weight. | Volume by experiment. | 1·225 as standard. | Volume by theory. | Specific gravity by experiment. | Specific gravity by theory. |
| Boracic acid ..... | $BO_3$ | 34·9 | 19·45 | 16 | 19·60 | 1·794 | 1·781 |
| Phosphoric acid... | $PO_5$ | 71·44 | 29·74 | 24½ | 30·01 | 2·387 | 2·381 |
| Silica ..... | $SiO_3$ | 46·22 | 17·37 | 14 | 17·15 | 2·660 | 2·695 |
| Alumina ..... | $Al_2O_3$ | 51·4 | 14·56 | 12 | 14·70 | 3·531 | 3·496 |
| Thoria..... | ThO | 67·6 | 7·19 | 6 | 7·35 | 9·402 | 9·197 |
| Glucina ..... | $G_2O_3$ | 77 | 25·66 | 21 | 25·72 | 3·000 | 2·993 |
| Yttria ..... | YO | 40·2 | 8·3 | 7 | 8·57 | 4·842 | 4·691 |
| Zirconia ..... | $Zr_2O_3$ | 91·4 | 21·2 | 18 | 22·05 | 4·300 | 4·145 |

## SECTION V.

### *Dimorphism and Polymorphism.*

In Section II. we pointed out distinct differences in the volumes of oxides before and after being heated, and we showed that these differences were either 1·225 or $\frac{1·225.}{2}$ The question therefore naturally arose—Is there any such difference between the volumes of bodies of the same composition but of unlike forms? If any such difference could be established, a flood of light would be thrown upon this obscure subject, and the alteration in properties would become at once comprehensible. Let us take some of the most noted examples of polymorphism and dimorphism to test this view.

*Example* I.—Carbon offers three very unlike forms and

conditions, the diamond, graphite and charcoal. The sp. gr. of diamond varies from 3·4 to 3·5, but as an average may be taken at 3·45. Graphite enjoys a sp. gr. of 2·5 according to Berzelius*; Karsten states it at 2·328, the mean gives 2·414. The purest charcoal obtained from alcohol has a sp. gr. of only 2·0.

Now assuming from the considerations deduced by Regnault from his experiments on specific heat, that the equivalent of carbon, 6·12, should be doubled to 12·24, we have the following simple relations:—

| | Vol. by experiment. | No. of vols. 1·225 as unity. | Vol. by theory. | Sp. gr. by experiment. | Sp. gr. by theory. |
|---|---|---|---|---|---|
| Alcohol-charcoal | 6·00 | 5 | 6·12 | 2·0 | 1·96 |
| Graphite . . | 4·97 | 4 | 4·90 | 2·414 | 2·448 |
| Diamond . . | 3·48 | 3 | 3·67 | 3·45 | 3·27 |

The result exhibited by this table is very striking, as it shows that the three forms of carbon differ from each other by one unit in volume, viz. 3, 4, 5, so that we may conceive the diamond to pass into the graphite by expanding one unit volume, and graphite into charcoal, by a similar expansion, or *vice versâ*, by condensation.

*Example* II.—As a second example we may take calc spar and arragonite, dimorphous forms of carbonate of lime, of which the following table gives the recorded specific gravities:—

| Calc spar. | | Arragonite. | |
|---|---|---|---|
| 2·718 | Brisson. | 2·995 | Breithaupt. |
| 2·778 | Baumgartner. | 2·931 | Mohs. |
| 2·727 | Baumgartner. | 2·946 | Beudant. |
| 2·6987 | Karsten. | Mean . | 2·957 |
| 2·7064 | Karsten. | | |
| 2·723 | Beudant. | | |
| Mean . 2·725 | | | |

Calculating the volumes on the equivalent 50·50, we have the following result:—

| | Vol. by experiment. | 1·225 as unity. | Vol. by theory. | Sp. gr. by experiment. | Sp. gr. by theory. |
|---|---|---|---|---|---|
| Calc spar | 18·53 | 15 | 18·37 | 2·725 | 2·749 |
| Arragonite | 17·08 | 14 | 17·15 | 2·957 | 2·945 |

Thus the same alteration of volume is exhibited here as in the previous example, the difference in this case also being one unit volume or 1·225. The experimental and theoretical results are sufficiently near when calculated on the mean specific gravity, but actually accord, if we assume that usually

* *Ann. der Chemie*, Bd. xlix. S. 250.

adopted for calc spar, viz. 2·75 according to Neumann, and 2·946 for arragonite according to Beudant.

*Example* III.—A notable instance of dimorphism is exhibited in iron pyrites, viz. in cubic iron pyrites, and in white pyrites or cockscomb spar.

According to Karsten, cubic iron pyrites has the sp. gr. 4·90, and Mohs states that of cockscomb pyrites to be 4·678. The volume calculated on the atomic weight is as follows:—

| | Vol. by exp. | No. of vols. | Vol. by theory. |
|---|---|---|---|
| Cubic pyrites . . | 12·28 | 10 | 12·25 |
| Cockscomb pyrites . | 12·87 | $10\frac{1}{2}$ | 12·86 |

The difference in this case is therefore $\frac{1\cdot225}{2}$; but if our view be correct, that the magnesian equivalents should be doubled, the number of volumes will be actually 20 for iron pyrites and 21 for cockscomb pyrites, making the difference of one unit volume or 1·225, as in the previous cases.

*Example* IV.—The sulphurets offer examples of unlike forms and allotropic conditions of the same substance. Black sulphuret of mercury has, according to our own experiments, a sp. gr. of 7·331, whilst, according to Musschenbroek and others, cinnabar enjoys a sp. gr. of 8·00. The volume calculated on the atomic weight, 117, is as follows:—

| | Volume by experiment. | No. of unit vols. | Vol. by theory. |
|---|---|---|---|
| Red sulphuret of mercury | 14·6 | 12 | 14·7 |
| Black sulphuret of mercury | 15·95 | 13 | 15·9 |

The difference in this case also is one unit volume or 1·225.

A relation is also shown between the native sesquisulphuret of antimony, with a sp. gr. of 4·62 according to Mohs, and of amorphous kermes, with sp. gr. 4·15 according to Gmelin.

| | Vol. by exp. | No. of unit vols. | Vol. by theory. |
|---|---|---|---|
| Native $Sb_2S_3$, $\frac{177\cdot5}{4\cdot62}$ | = 38·42 | $31\frac{1}{2}$ | 38·59 |
| Kermes . $\frac{177\cdot5}{4\cdot15}$ | = 42·77 | 35 | 42·87 |

The difference in this case being $3\frac{1}{2}$ volumes.

*Example* V.—The researches of Rose have thrown much light on the difference in specific gravity between the varieties of titanic acid. Thus we have—

| | | |
|---|---|---|
| Artificial $TiO_2$ sp. gr. | 3·66 Rose. | |
| Anatase . . . . | 3·912 Rose. | 3·85 |
| | 3·927 Rose. | |
| | 3·829 Mohs. | |
| | 3·759 Breithaupt. | |
| | 3·826 Mohs. | |
| Brookite . . . . . | 4·128 Rose. | |
| Rutil . . . . . | 4·256 Rose. | |

These differences are very notable, and when calculated on the generally received atom of titanic acid, 40·33, viewing it as $TiO_2$, we obtain the following relations:—

| | Vol. by exp. | No. of vols. | Vol. by theory. |
|---|---|---|---|
| Artificial $TiO_2$ | 11·01 | 9 | 11·02 |
| Anatase . . | 10·48 | $8\frac{1}{2}$ | 10·41 |
| Brookite . . | 9·77 | 8 | 9·80 |
| Rutil . . . | 9·47 | $7\frac{3}{4}$ | 9·49 |

The relations here are very striking, but at the same time give rise to new questions. We have previously seen repeated examples of a volume represented by $\frac{1\cdot225}{2}$, but this is the first instance of $\frac{1\cdot225}{4}$. Are we to admit the subdivision of the volume 1·225? It may be necessary to do so, but not on an isolated case like the present. May we not rather suppose that the contraction of volumes takes place on associated atoms? Thus—

| | | | | |
|---|---|---|---|---|
| 1 eq. $TiO_2$ | contracting | 1 unit volume | forms | Brookite. |
| 4 | ... | 1 unit volume | ... | Rutil. |
| 2 | ... | 5 unit volumes | ... | Anatase. |

Which of these hypotheses is right it is impossible to say in the present state of our knowledge; but we do not feel warranted in admitting a further division of 1·225 on a single case, although we by no means deny that such division may afterwards become necessary, especially as far as regards $\frac{1\cdot225}{2}$.

*Example* VI.—*Quartz and Opal.* Silica presents two well-defined forms in quartz and anhydrous opal, the sp. gr. of the former being 2·66, while the anhydrous opal analysed by Klaproth possesses the sp. gr. 2·072.

| | | Vol. by exp. | 1·225 as unity. | Theory. |
|---|---|---|---|---|
| Quartz | $\frac{46{\cdot}22}{2{\cdot}66} = 17{\cdot}3$ | | 14 | 17·15 |
| Opal | $\frac{46{\cdot}22}{2{\cdot}072} = 22{\cdot}3$ | | 18 | 22·05 |

The difference in this case is 4v.

*Example* VII.—*Alumina* forms a similar instance:—

| | | Vol. by exp. | 1·225 as unity. | Theory. |
|---|---|---|---|---|
| Ruby . . . | $\frac{51{\cdot}4}{3{\cdot}531} = 14{\cdot}56$ | | 12 | 14·70 |
| Ignited alumina | $\frac{51{\cdot}4}{4{\cdot}15} = 12{\cdot}38$ | | 10 | 12·25 |

The difference is 1·225 × 2. Numerous other instances of this uniformity of difference might be cited if necessary.

*Example* VIII.—*Elementary allotropism.* In the metals we have several well-marked instances of elementary allotropism. Thus Berzelius, in his memoir on allotropism, has pointed out that iridium artificially prepared has a sp. gr. not exceeding 16·0, while the native metal enjoys a sp. gr. approaching to that of platinum.

The most uniform results for native metallic iridium are as follows:—

| | |
|---|---|
| 19·5 | Mohs. |
| 18·68 | Children. |
| 22·1 | Breithaupt. |
| Mean . . 20·09 | |

Hence we have for native iridium $\frac{98{\cdot}84}{20{\cdot}09} = 4{\cdot}92$, and for the metal as obtained by reduction, $\frac{98{\cdot}84}{16{\cdot}0} = 6{\cdot}18$.

| | Exp. | No. of vol. | Theory. |
|---|---|---|---|
| Native iridium . | 4·92 | 4 | 4·90 |
| Reduced iridium | 6·18 | 5 | 6·12 |

In this case, therefore, we have the variation of one unit volume between the two different states of the metal.

*Example* IX.—*Osmium* presents a similar uniformity in the difference between its three states. Thus, according to Thenard, wrought osmium has a sp. gr. of 19·5, while that reduced from the oxide has a sp. gr. of only 10·0 according to Berzelius, and when obtained by heating its amalgam 7·000.

| | Exp. | No. of vol. | Theory. |
|---|---|---|---|
| $\frac{99{\cdot}97}{19{\cdot}5}$ | $= 5{\cdot}12$ | 4 | 4·9 |
| $\frac{99{\cdot}97}{7{\cdot}0}$ | $= 14{\cdot}28$ | 12 | 14·70 |
| $\frac{99{\cdot}97}{10{\cdot}0}$ | $= 9{\cdot}99$ | 8 | 9·8 |

*Example* X.—*Platinum* exhibits several very decided allotropic differences. Thus in its densest state it has sp. gr. 23·5 (Cloud); after fusion the sp. gr. is 20·3 (Brisson); the powder obtained by heating the oxide enjoys sp. gr. 17·76 (P. and J.), while platinum black has sp. gr. 16·557 (Liebig).

| | | Expt. | | Theory. |
|---|---|---|---|---|
| Platinum black | $\frac{98{\cdot}8}{16{\cdot}557}$ | $= 5{\cdot}97$ | 5 | 6·12 |
| Platinum powder | $\frac{98{\cdot}8}{17{\cdot}76}$ | $= 5{\cdot}56$ | $4\frac{1}{2}$ | 5·51 |
| Platinum after fusion | $\frac{98{\cdot}8}{20{\cdot}3}$ | $= 4{\cdot}86$ | 4 | 4·9 |
| Platinum hammered | $\frac{98{\cdot}8}{23{\cdot}5}$ | $= 4{\cdot}24$ | $3\frac{1}{2}$ | 4·28 |

These numbers, and those deduced from the allotropic conditions of osmium and iridium, offer much confirmation of the view which we are inclined to entertain, that the attraction of cohesion is itself governed by the volume 1·225. Another instance of this contraction is seen in palladium, which in its usual state possesses sp. gr. 10·923, but when hammered attains sp. gr. 12·14.

| | Exp. | | Theory. |
|---|---|---|---|
| $\frac{53{\cdot}3}{10{\cdot}923}$ | $= 4{\cdot}88$ | 4 | 4·9 |
| $\frac{53{\cdot}3}{12{\cdot}14}$ | $= 4{\cdot}39$ | $3\frac{1}{2}$ | 4·29 |

The differences between the theoretical and experimental numbers are not greater than can be accounted for by the uncertain atomic weight. The very numerous instances of a change of volume consequent on the combination of the elements may all be brought to reinforce this part of our argument. For instance, in the case of lead uncombined we find a volume of 8v, but when combined with sulphur a volume of 6v. Nay more, it appears from our former as well as the present paper, that the volume of an element is frequently actually merged. Such facts lead us to hope for the discovery

of far more wonderful examples of allotropism than those we have already given.

Berzelius has thrown out the suggestion that the presence of the different forms of the radical may account for allotropism in their compounds, and our researches go far to prove this sagacious view. We had intended to have devoted ourselves to further proofs of this theory, but our memoir has already reached an unreasonable length and we must defer the subject.

We have, however, one other notable instance of allotropism to which we must refer. SULPHUR exists in several distinct states: in the first state, that of native sulphur, we have the following determinations:—

| | |
|---|---|
| 2·033 | Brisson. |
| 2·050 | Karsten. |
| 1·989 | Karsten. |
| 1·898 | Fontenelle. |
| 2·072 | Mohs. |
| 2·027 | Osann. |
| 2·066 | Marchand and Scheerer. |
| Mean . . 2·019 | |

This result agrees very closely with our own determination, 2·010 (see Section I.).

The specific gravity of waxy sulphur procured by pouring viscid melted sulphur into water, is 1·959 according to Marchand and Scheerer; according to our own experiments 1·921; the mean being 1·940. The other estimations by ourselves we have described in a previous section, and we now find the following relations:—

| | Volume by experiment. | No. of 1·225 vol. | Volume by theory. | Specific gravity by experiment. |
|---|---|---|---|---|
| Sulphur in viscid melted state ... | 9·17 | $7\frac{1}{2}$ | 9·18 | 1·748 |
| Sulphur in clear amber liquid ... | 8·87 | $7\frac{1}{4}$ | 8·88 | 1·807 |
| Sulphur in flowers ..... | 8·38 | 7 | 8·57 | 1·913 |
| Sulphur in soft state ..... | 8·26 | $6\frac{3}{4}$ | 8·27 | 1·940 |
| Sulphur in crystals from fusion... | 7·97 | $6\frac{1}{2}$ | 7·96 | 2·010 |

The results of the above table afford the most powerful argument for the assumption of a volume $\frac{1\cdot225}{4}$ that we have yet seen. But still we adhere to our primitive volume 1·225, believing that a contraction of whole volumes of 1·225 may take place on associated atoms, as we alleged in the case of titanic acid.

TABLE IX.—Showing the Simple Relation in Volumes between unlike forms of the same body.

| Designation. | | | Volumes. | | | | |
|---|---|---|---|---|---|---|---|
| Name. | Formula. | Atomic weight. | Volume by experiment. | 1·225 taken as standard. | Volume by theory. | Specific gravity by experiment. | Specific gravity by theory. |
| Charcoal | $C_2$ | 12·24 | 6·12 | 5 | 6·12 | 2·0 | 2·0 |
| Graphite | | | 4·90 | 4 | 4·90 | 2·5 | 2·5 |
| Diamond | | | 3·50 | 3 | 3·67 | 3·5 | 3·33 |
| Calc spar | $CaO, CO_2$ | 50·50 | 18·53 | 15 | 18·37 | 2·725 | 2·749 |
| Arragonite | | | 17·08 | 14 | 17·15 | 2·957 | 2·945 |
| Cockscomb pyrites | $FeS_2$ | 60·0 | 12·87 | 10½ | 12·86 | 4·678 | 4·664 |
| Cubic pyrites | | | 12·28 | 10 | 12·25 | 4·90 | 4·897 |
| Black sulph. mercury | HgS | 117 | 15·95 | 13 | 15·90 | 7·331 | 7·358 |
| Cinnabar | | | 14·6 | 12 | 14·7 | 8·001 | 7·959 |
| Artificial kermes | $Sb_2S_3$ | 177·5 | 42·77 | 35 | 42·87 | 4·15 | 4·140 |
| Native kermes | | | 38·42 | 31½ | 38·59 | 4·62 | 4·600 |
| Titanic acid | $TiO_2$ | 40·33 | 11·01 | 9 | 11·02 | 3·66 | 3·659 |
| Anatase | | | 10·48 | 8½ | 10·41 | 3·85 | 3·874 |
| Brookite | | | 9·77 | 8 | 9·8 | 4·128 | 4·115 |
| Rutil | | | 9·47 | 7¾ | 9·49 | 4·256 | 4·249 |
| Anhydrous opal | $SiO_3$ | 46·22 | 22·3 | 18 | 22·05 | 2·072 | 2·096 |
| Quartz | | | 17·3 | 14 | 17·15 | 2·660 | 2·695 |
| Ruby | $Al_2O_3$ | 51·4 | 14·56 | 12 | 14·70 | 3·531 | 3·496 |
| Ignited alumina | | | 12·38 | 10 | 12·25 | 4·150 | 4·195 |
| Reduced iridium | Ir | 98·84 | 6·18 | 5 | 6·12 | 16·0 | 16·15 |
| Native iridium | | | 4·99 | 4 | 4·90 | 20·09 | 20·17 |
| Osmium from amalgam | Os | 99·97 | 14·28 | 12 | 14·70 | 7·0 | 6·721 |
| Reduced osmium | | | 9·92 | 8 | 9·8 | 10·0 | 10·20 |
| Native osmium | | | 5·12 | 4 | 4·9 | 19·5 | 20·40 |
| Platinum black | Pt | 98·8 | 5·97 | 5 | 6·12 | 16·557 | 16·143 |
| —— powder | | | 5·56 | 4½ | 5·51 | 17·760 | 17·931 |
| —— after fusion | | | 4·86 | 4 | 4·9 | 20·300 | 20·163 |
| —— hammered | | | 4·20 | 3½ | 4·28 | 23·500 | 23·084 |
| Sulphur in viscid melted state. | S | 16·03 | 9·17 | 7½ | 9·18 | 1·748 | 1·746 |
| Sulphur in clear amber melted | | | 8·87 | 7¼ | 8·88 | 1·807 | 1·805 |
| Sulphur in flowers of | | | 8·38 | 7 | 8·57 | 1·913 | 1·870 |
| Sulphur in soft state | | | 8·26 | 6¾ | 8·27 | 1·940 | 1·938 |
| Sulphur in crystals from fusion | | | 7·97 | 6½ | 7·96 | 2·010 | 2·013 |

## *Conclusion.*

We have now to sum up the results of the previous researches, which we announce generally under the following proposition:—

I. *The volumes of solid bodies bear a simple relation to each other, being multiples of a sub-multiple of the volume of ice, which for convenience is adopted as a standard.*

*a.* The force of cohesion in the metals prevents the assumption of their natural volumes, which however appear when they are placed in a position not to yield to the solicitation of cohesion.

*b.* It is probable that the differences from the natural volume produced by cohesion can be expressed by a sub-multiple of the volume of ice.

*c.* The differences between unlike forms, of dimorphous, polymorphous, and allotropic substances, are expressed by a sub-multiple of the volume of ice.

The results to which we were led by our previous researches now become intelligible. We then asserted that the volumes of salts were multiples of 9·8 or of 11. We guarded ourselves against stating that the latter number was absolutely 11, but we averred it to be "a number very nearly approaching the number 11." We now know exactly what that number is, and see its relation to 9·8 or the volume of ice—

$$9{\cdot}8 + \frac{9{\cdot}8}{8} = 11{\cdot}025,$$

a number very nearly approaching 11. We have shown in this memoir that 9·8 is composed of 1·225 × 8, and in the same way 11 is 1·225 × 9. That we should have assumed 11 as the unit volume for salts when we were ignorant of its root, is not surprising, considering its frequent occurrence in salts.

Thus if Rv be the volume of any radical, Ov that of oxygen, and Av of an acid, the general formula Rv + Ov + Av = Xv will apply to a large class of salts divisible by the number 11, although the latter number itself is a multiple of 1·225. The magnesian sulphates have a volume of 22 according to our former paper. By the results in this paper, the volume of sulphur in its solid state, as flowers of sulphur, is 8·57. Oxygen we found in most cases to have a volume of 1·225 × 2; hence $SO_3$ will be Sv + Ov × 3 = 15·92. The magnesian metals were shown to have a volume of 1·225 × 3, hence their oxides, as shown also by experiment, have a volume = Rv + Ov = 6·12.

| | |
|---|---|
| RO . . . . . | 6·12 |
| $SO_3$ . . . . . | 15·92 |
| $RO, SO_3$ . . . | 22·04 |

So that we are conducted by entirely different considerations to the same result which we gave in Table VII. of our former memoir. We stated at Table VI. of that series of researches, that $KO, SO_3$ had a volume of 33·05. By Table V. of the present paper KO is shown to have a volume of 17·15. $SO_3$ we have just shown to have 15·92.

| | |
|---|---|
| KO . . . . . | 17·15 |
| $SO_3$ . . . . . | 15·92 |
| KO, $SO_3$ . . . | 33·07 |

a result almost identical with that given, and warranting the numbers 11 × 3. We pointed out at the same time that NaO $SO_3$ differed from this law, but the apparent exception is now explained. Our sp. gr. for this salt, 2·597, gave the volume 27·5; Karsten's result then referred to, 2·631, gave the volume 27·14. Now by Table V.—

| | |
|---|---|
| NaO . . . . | 11·025 |
| $SO_3$ . . . . | 15·92 |
| | 26·945 |

The curious class of chromates find now a complete elucidation. Chromium possesses an atomic volume 4·9 (Table I.), while O in the acids occasionally has a volume of 4·9,—

$$\mathrm{Crv} + \underline{\mathrm{O}}\mathrm{v} \times 3 = 19{\cdot}6$$

the exact number which we found by experiment for $CrO_3$ in our former paper. KO, $CrO_3$ ought to be as follows:—

| | |
|---|---|
| KO . . . | 17·15 |
| $CrO_3$ . . . | 19·6 |
| KO, $CrO_3$ . | 36·75 |

the number which we found being 37·1, a result we then allowed as difficult to be explained. On KO, $2CrO_3$ we find an increase of 1·225 above the second atom of $CrO_3$, due perhaps to the dimorphous relations of chromium. The results as then found, and those calculated according to our advanced knowledge in the present paper, are as follow*—

| | Vol. found. | Theory. |
|---|---|---|
| KO, $CrO_3$ . . . | 37·1 | 36·75 |
| KO, $2CrO_3$ . . . | 57·8 | 57·57 |
| KO, $3CrO_3$ . . . | 76·8 | 77·17 |

Finally, let us take the singular results obtained for the carbonates as a test of this view. We found a sp. gr. for KO, $CO_2$ of 2·103, which is too low a number when compared with the only other recorded result, that of Gmelin, 2·264. The latter gives the atomic volume $\frac{69{\cdot}4}{2{\cdot}264} = 30{\cdot}65$.

* We avail ourselves of this opportunity to correct an error into which we fell in our former paper. We there stated that KO, $2CrO_3$ was not reduced to KO, $CrO_3$ by litharge, but formed a compound 2KO, $3CrO_3$. By continued action, however, the bichromate is wholly reduced to yellow chromate, and we are therefore satisfied that what we described as 2KO, $3CrO_3$, was merely a mixture of KO, $CrO_3$ and KO, $2CrO_3$.

Deducting 17·15 for KO, we have a volume of 13·5 for $CO_2$. The volume of $KO, CO_2 + HO\,CO_2$, according to Gmelin's results and our own, was 49·0, from which 30·65 must be deducted for $KO, CO_2$ and 4·9, as in the case of many hydrates, for combined water. The difference, 13·45, is the volume of $CO_2$ in bicarbonate of potash. Carbonate of soda we found to possess a sp. gr. 2·427, which agrees very well with Karsten's result, 2·465. From the resulting volume, 22·0v, must be deducted 11v for the volume of soda, leaving 11v for $CO_2$. $NaO, CO_2 + HO, CO_2$ had a volume of 38·6, from which must be deducted 22·05 + 4·9, for reasons above stated, leaving 11·65 for $CO_2$. Here then we have—

$CO_2$ in the carbonate of potash = 13·45
$CO_2$ ... ... soda . = 11·65

These differences are therefore connected with the character of the base itself. Are the differences due to the allotropic condition of carbon? does $CO_2$ in the potash salts contain charcoal carbon? and in the soda salts graphit carbon? does the denser form cause the volume of oxygen itself to become condensed? and may we thus explain the differences of calc spar and arragonite? These are questions which shall be answered in a future memoir.

At present the examples above given may suffice for illustrations of the accuracy of the standards which we took in our former paper. We reserve for a distinct memoir, the important considerations which flow from our present results with regard to the constitution of salts, and the behaviour of the water entering into their constitution.

It would be easy to give a classification of the metals from the views developed in the preceding sections, were it not that their allotropic conditions associate the groups by a distinct chain of connection. We intend to follow up this paper with another, in which we shall endeavour to show that the elements, not only in their natural states, but even in their unusual forms, may be brought under one simple mathematical law, thus clearly proving that sufficient grounds exist for the acceptance of the law which we have tried to establish in the present memoir,—THAT THE ATOMIC VOLUMES OF BODIES STAND IN A SIMPLE MULTIPLE RELATION TO EACH OTHER.

March 2, 1846.—The President in the Chair.

Mr. Nesbitt presented his Essay "On the Analysis of the Hop, and the Nature of the Manures beneficial to its Growth."

The following papers were read:—

## CLXII. *On the Influence exerted by Electricity, Platinum and Silver upon the Luminosity of Phosphorus.* By Dr. C. F. Schœnbein.

SOME time ago I tried to show that the shining of phosphorus in atmospheric air is intimately connected with the formation of that highly oxidizing agent I have called ozone. The correctness of that view is confirmed by the fact that phosphorus never becomes luminous if the production of ozone be prevented, or that luminous phosphorus grows dark if the ozone be removed. It is well-known that phosphorus remains dark at low temperatures, and I have ascertained that under these circumstances no ozone is produced; my experiments have further shown that phosphorus still shines in ozonized air at a temperature at which in pure air phosphorus exhibits not the slightest emission of light.

According to the results of my former researches, ozone is formed during electrical discharges taking place in atmospheric air, the electrolysis of water and the action exerted by phosphorus upon moist mixtures of oxygen and nitrogen, oxygen and hydrogen, oxygen and carbonic acid gas.

These facts taken together led me to suspect that phosphorus might become luminous in atmospheric air within which electrical discharges had been effected, at a temperature at which phosphorus does not shine in common air. How far that conjecture is well-founded will appear from the facts I am going to state.

1. If, at a temperature of 2° to 5° R. below zero, a piece of phosphorus, about an inch long, and having a clean surface, be laid upon a wooden board, and the free end of a metallic wire connected at its other end with the conductor of an electrical machine be placed at the distance of a few lines before the dark phosphorus, the latter will become luminous as soon as the electrical brush makes its appearance at the free end of the wire; and in addition, a luminous tail of 4 to 6 inches long will be perceived behind the phosphorus. The brush is no sooner made to disappear than the shining tail disappears also, whilst the phosphorus itself remains luminous for a second or two more. The brush being called forth again, the phænomena described will repeatedly take place.

2. The same piece of phosphorus, at a temperature of about 4° R. below zero, being placed within a coil made up of one extremity of a copper wire, so that the end of that coil projects (in the shape of a point) about a line beyond the phosphorus, and the other end of the wire being connected with the conductor of the electrical machine, a very interesting phænomenon will take place as soon as the brush is caused to appear at the metallic point that projects beyond the phosphorus. From the centre of the brush proceeds a luminous cone, the apex of which lies in the middle of the brush. The length of that cone varies with the size of the brush, the longer the latter the longer the cone. I have often obtained cones at least two feet in length with brushes being hardly an inch long. I am sure the admirable machine of the Polytechnical Institution would yield tails of extraordinary length, and it is really worth while to make the experiment with that powerful apparatus. I must not omit to mention that the phænomenon resembles exactly the tail of a comet, and cannot be perceived but in complete darkness; but it is hardly necessary to add that the luminous cone disappears invariably and simultaneously with the brush. If the finger be approached to the brush so as to change the position of the latter, the cone in its whole length is also put in motion. In the experiments described use was made of the positive brush; in changing the positive electricity for the negative a tail is likewise obtained, but that cone is thin and less lively.

3. If, at a temperature of 2° R. below zero, a piece of phosphorus be placed in a bottle so arranged that the electrical brush may at pleasure be produced within that vessel, the phosphorus becomes luminous so soon as the brush makes its appearance, and that phosphorescence is the more lively the stronger the brush and the longer the latter had been made to play. The emission of light continues for a short time to take place after the cessation of the play of the brush. The phosphorus having grown dark, becomes luminous again along with the reappearance of the brush.

4. According to my experiments, chemical and voltaic ozone are instantaneously destroyed by a number of gaseous substances, *ex. gr.* by olefiant gas, sulphurous acid, fumes of hyponitric acid, vapour of æther, &c. Hence it comes that phosphorus placed in atmospheric air, mixed up with small quantities only of any of the substances named, does not produce ozone, and it is well known that phosphorus remains dark under the same circumstances. If the experiment be made as indicated under § 3, the electrical brush, lively as it

may happen to play within the air of the bottle, does not call forth in phosphorus the slightest sign of phosphorescence, provided the atmospheric air surrounding phosphorus contain some olefiant gas, hyponitric acid, &c.

5. Some time ago I ascertained the fact that either platinum black or spongy platinum has the power of destroying indigo, of colouring blue the resin of guaiacum, of decomposing iodide of potassium, in short, of producing oxidizing effects very similar to those brought about by the electrical brush or spark. That similarity of action made me suspect that, with regard to phosphorus, platinum being in a state of minute mechanical division, might conduct itself like electricity, and the results of my experiments have proved the correctness of my conjecture. At a temperature of 4° R. below zero, newly-prepared platinum black was placed upon a watch-glass; now, as soon as a piece of phosphorus (having previously been wiped off with filtering-paper) was made to touch the metallic powder it became luminous, first at the point of contact, and immediately afterwards along its whole surface. On breaking that contact, the phosphorus turned dark again.

6. Spongy silver, as it is obtained from the acetate of that metal, acts upon phosphorus as powerfully as spongy platinum does; for no sooner has phosphorus been touched by that silver than the former becomes luminous, even at a temperature of 6° R. below zero.

7. Iron, lead, copper, antimony, bismuth, tin, being in a state of minute mechanical division, have no effect upon phosphorus. With gold, iridium, and the rest of the metals, I have not yet made any experiment.

---

## CLXIII. *On Struvite, a new Mineral.* *By* G. L. Ulex.

NUMEROUS crystals were found in digging out the ground of St. Nicholas church, in the middle of our town; the largest of which are about one inch long, and weigh from 1·4 to 1·8 grm. Their primary form is a right rhombic prism. [The admeasurements were made by Prof. Marx.]

| | |
|---|---|
| M on M . . . | 95° 10′ |
| M on O . . . | 132° 25′ |
| O on P . . . | 138° 25′ |
| *s* on *s* . . . | 63° 30′ |
| *h* on *t* . . . | 143° |
| *h* on *h* . . . | 57° 10′ |

Fig. 1.

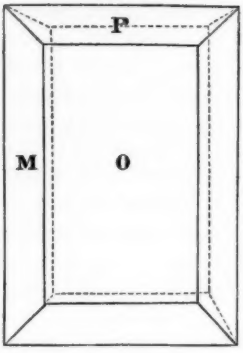



Fig. 4.




Fig. 2.

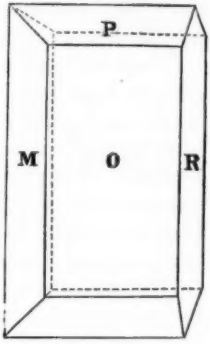



Fig. 5.

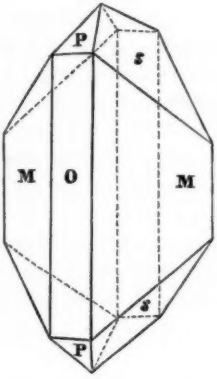



Fig. 6.

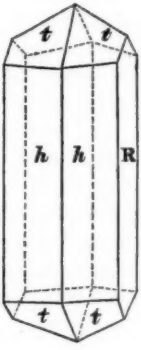



Fig. 7.

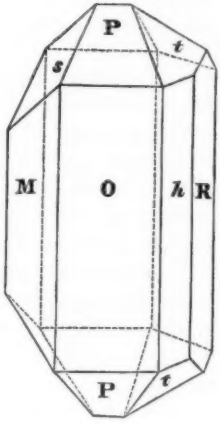



*Fig.* 1. Represents a crystal of struvite in its simplest form.

*Fig.* 2. The crystal as it most frequently occurs.

*Fig.* 4. A segment.

*Figs.* 5, 6. Crystals with some secondary planes, but generally only segments occur; the plane *s* on both sides large and distinct: the planes *h* and *t* very small.

*Fig.* 7. A view of the planes collectively as exhibited by some crystals.

They cleave parallel to the plane of O. A peculiarity in these crystals is, that they occur almost always in halves, and appear to have rested or been formed on planes which would have passed through the centre of the entire crystal. One of these natural segments is shown in fig. 2.

The crystals are transparent, and of a somewhat yellow colour; most of them inclose organic matter, and are thereby

rendered more or less dark and opake. They are harder than talc, but are scratched by gypsum. Their specific gravity is 1·7.

They are very sparingly soluble in water, and in consequence tasteless. When heated in a tube they give out much water and ammonia (the black crystals empyreumatic water and ammonia) without flying into pieces. When heated to redness, they exhibit the phænomenon of phosphorescence: the passing of *c* into *b*, phosphoric acid. Heated before the blowpipe they melt into a colourless glass, which on cooling forms a white enamel.

The constituent parts of the salt are phosphoric acid, magnesia, ammonia and water.

Dissolved in hydrochloric acid and precipitated by ammonia, they yield a sandy powder, which under the microscope exhibits the well-known form of the phosphate of ammonia and magnesia.

The salt loses by ignition 54·7 to 55·5 per cent. (the difference is caused by the small quantity of organic matter). The ammonia was estimated by means of the chloride of platinum; by dissolving the salt in hydrochloric acid, 6·9 to 7·1 per cent. of ammonia were found. The residue of 44·5 to 45·3 per cent. should be the same combination of phosphoric acid with magnesia as is contained in the phosphate of magnesia and ammonia, because if the crystals are dissolved in hydrochloric acid and precipitated by ammonia, the fluid which is filtered from the precipitate gives no reaction either with sulphate of magnesia or with phosphate of soda. It consists therefore of

$$(NH_4O) + 2MgO + PO^5) + 12HO.$$

The crystals are the same salt which is found in many animal secretions, and in putrifying urine.

The salt is not altered by the air. Mr. Graham has informed us, that if the artificial salt is heated to 212° F. it loses 10 at. of water and no ammonia. The natural crystals can bear a temperature of 248° F., and they give out the same quantity of water and no ammonia. The products of distillation were conducted into a solution of the nitrate of the protoxide of mercury, which was not blackened.

Concerning the locality where the crystals are found, we perceive below the upper strata, at a depth of 6 to 12 feet, a large quantity of cattle-dung mixed with straw, in a state of putrefaction. This passes by degrees into a black peat earth, which extends to a depth of 26 feet and rests upon gravel. The peat earth, of a thickness of 10 to 12 feet, consists of a homogeneous impalpable mass, mixed here and there with

small parts of vegetable remains (parts of grasses; Sphagnum and other mosses could not be detected). This is the true matrix of the crystals, in which here and there blue iron earth (protophosphate of iron or vivianite) is also found.

By drying in the air it loses 40–50 per cent. of water, and is not to be distinguished from the heavy black turf.

Water dissolves very little from it. The solution is of a light brown colour, without any reaction upon litmus. Heated, it gives off at first some ammonia; in other respects it smells and burns like turf, with a bright flame. The ashes which remain vary in weight from 20–30 per cent.; moistened with water it does not act upon litmus.

A quantity dried at 212° F. was subjected to analysis; 100 parts of it gave—

| | | |
|---|---|---|
| 2·0 | per cent. | soluble in æther (principally chlorophylle). |
| 1·5 | ... ... | alcohol (principally resinous matter). |
| 1·5 | ... ... | water (principally salts of humous acids). |
| 36·0 | ... ... | liquor potassæ (principally humous acids). |
| 36·0 | ... | organic residue (principally humine and vegetable fibrine). |
| 23·0 | ... | inorganic residue, consisting of— |
| 0·3 | ... | soluble in water (sulphate of potass and chloride of sodium, no phosphates of alkali). |
| 11·5 | ... | soluble in hydrochloric acid (principally alumina and phosphate of magnesia and lime, less peroxide of iron and sulphate of lime). |
| 12·2 | ... | insoluble in hydrochloric acid (sand; calcined with soda and decomposed by hydrochloric acid, it gave 11 silica, 1·2 alumina, and peroxide of iron). |

The analysis shows that we have a humous mass, which has been formed from organic matters by putrefaction and decay. It is probable that these matters were principally the excrements of Herbivora; a presumption which is supported by the analysis of the ashes, from the quantities of phosphate of magnesia and lime.

The solid excrements of the Herbivora are characterized by abundance of phosphate of magnesia, and the deficiency of ammoniacal salts; the fluid excrements (urine) have, on the contrary, abundance of ammoniacal salts (from the decomposition of urea) and are deficient in earthy salts; relations which make it probable that the formation of such large crystals in such quantities (they occur in thousands) was caused

by a reaction of the urine upon the solid excrements, where the first gave the ammonia, the latter the phosphate of magnesia.

The locality where the crystals are found confirms this assumption. The place where St. Nicholas's church is built was occupied 800 years ago by the New Castle (Neue Burg), which was burnt and destroyed with the whole city of Hamburg, in 1072, by Kruko, tyrant of the Wenden. Now it is most probable that the ditch of the castle was used as a reservoir for rubbish and manure by the inhabitants of the new-built city, who preferred trade, as more profitable, to agriculture. So by degrees the ditch was filled, and covered partly with houses, and a small part of it formed till a late period an open dung-pit, which was emptied from time to time. The crystals are found principally below the dung-pit, and appear to be formed by the infiltration of urine through a soil consisting of vegetable matters.

The crystals forming a mineral which has never yet been described, are named Struvite, in honour of the minister Von Struve, well known to mineralogists, and highly meritorious from the great interest he takes in the advancement of science in the town of Hamburg.

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March 16, 1846.—The President in the Chair.

Mr. Robert Porrett presented to the Museum a specimen of Sulphocyanide of Copper, prepared by him in 1816.

Mr. Thomas Taylor presented a copy of his papers "On some New Species of Animal Concretions," and "On some New Species of Biliary and Intestinal Concretions."

Charles Oakes, Esq., and Thomas Taylor, Esq., were elected Members.

The following papers were read:—

"Reply to the Observations of M. Pierre on the Proportion of Water in the Magnesian Sulphates and Double Sulphates," by Thomas Graham, Esq.

Mr. Warren De la Rue described a new body which he had obtained from cochineal, a subject he has been for some time past investigating, and which bears a remarkable similarity to a substance which Liebig has lately produced by the action of potassa on caseine, to which he assigns the composition $C_{16}$, N, $H_9$, $O_5$, at the same time stating that the formula requires confirmation. Though the analyses of the new substance differ somewhat from this formula (its composition appearing to be $C_{18}$, N, $H_{11}$, $O_6$), yet the agreement of its properties with those assigned by Liebig to the substance described by him, leaves but little doubt as to the identity of the two bodies.

A specimen of Liebig's substance, furnished by Dr. Hofmann, agrees perfectly in its physical characters.

The new body is obtained from cochineal by the following means:—The colouring principle being first separated from an infusion of cochineal, the mother-liquor is to be carefully evaporated in a water-bath to the consistence of a syrup, when there appears floating in it a small quantity of granular chalky-like masses, which being collected on a filter is kept warm, and, when drained, well-washed with cold water; they are then dissolved in boiling water and recrystallized; again well-washed, and finally dissolved in as small a quantity of boiling water as possible; a little animal charcoal is to be added, and the ebullition continued for a short time; on filtration and cooling, the new body crystallizes as a bulky assemblage of tufts, filling the vessels; on drying they form into paper-like masses, of a perfectly white colour and a beautiful silky lustre.

This body is sparingly soluble in cold water, considerably more so in hot water; soluble in ammonia, from which it crystallizes as the ammonia is driven off by heat; it is likewise soluble in acids.

From the process pursued in separating this substance from cochineal there is no doubt that it pre-exists, and is not produced by the operation; it may, however, be a product of oxidation of some part of the insect during its preparation for commerce. Three hundred parts of cochineal yield one part of the new body.

## CLXIV. *On Nitraniline, a new Product of Decomposition of Dinitrobenzol.* *By* James Sheridan Muspratt, *Ph.D.* *and* Augustus William Hofmann, *Ph.D.*

A GREAT number of investigations have proved that the action of nitric acid upon organic bodies produces changes in their composition in two ways. First, there is sometimes simply an accession of oxygen to the elements of the organic matter, the nitric acid being reduced to nitric oxide or nitrous acid and expelled. Thus, by treating *indigo* with nitric acid it becomes converted into *isatine*, the composition of which differs from that of indigo only by containing two equivalents of oxygen more than the latter. *Cinnamic acid* passes into *hydride of benzoyle*, water being formed, and the excess of carbon, combining with the oxygen of the nitric acid, escapes in the form of carbonic acid. By a further supply of oxygen the hydride of benzoyle is converted into *benzoic acid*. In all other cases the action of nitric acid differs in no respects from that of other means of oxidation, *ex. gr.* chromic acid, peroxide of manganese and sulphuric acid, &c.

The action of nitric acid however upon organic matters is in other cases more complex; it does not consist solely in the supply of oxygen, but besides that element, nitrogen also

enters into the newly-formed compound. *Indigo,* subjected for a long time to the action of concentrated nitric acid, undergoes a series of metamorphoses, and the last product which is formed, namely, *carbazotic acid* (nitrophenisic acid), contains to the same quantity of carbon a much larger proportion of nitrogen than the indigo from which it is derived.

*Cinnamic acid, hydride of benzoyle,* and *benzoic acid,* none of which contain nitrogen, furnish, as the last product of the action of nitric acid, a nitrogenous acid, which is known as *nitrobenzoic* (*nitrobenzinic*) *acid.*

A great many of the nitrogenous compounds produced in this manner possess the properties of acids. Besides the above-mentioned we might enumerate *nitrocinnamic acid, nitrosalicylic acid* (anilic acid), and many others similarly constituted. Some chemists have on this account, without hesitation, assumed the presence of nitric acid in these bodies. Berzelius represents the carbazotic acid as a copulated compound of hydrated nitric acid with a sort of saline body, in which another equivalent of nitric acid is combined with an organic oxide having the formula

$$C_{12} H_2 NO_3.$$

Carbazotic acid is therefore a copulated acid of similar constitution with the sulphovinic acid (bisulphate of oxide of ethyl), and would be represented as follows:—

$$C_{12} H_2 NO_3, NO_5 + HO, NO_5.$$

Also, in the other acids of this nature, which contain only *one* equivalent of nitrogen, Berzelius assumes the presence of nitric acid. According to his view, nitrobenzoic and nitrosalicylic acids would be represented as follows:—

Nitrobenzoic acid . . $C_{14} H_4 O_2 + HO, NO_5$
Nitrosalicylic acid . . $C_{14} H_8 O_4 + HO, NO_5$

There is no direct proof for this assumption, and therefore other chemists believe that the nitrogen in these compounds does not exist as nitric acid but as nitrous acid, $NO_3$; thus nitrobenzoic acid, according to Mulder, is $C_{14} H_4 O_4, HO, NO_3$. The compounds produced by the contemporaneous action of nitrogen and oxygen upon organic bodies are however not always acid; a great class of bodies furnish under such circumstances products in which the acid properties of the nitric acid have entirely disappeared: to these belong a number of organic bodies, which consist only of carbon and hydrogen. For example, if *benzol* is brought into contact with fuming nitric acid, they combine with separation of water and form

an indifferent body, *i. e.* nitrobenzol (nitrobenzide) discovered by Mitscherlich.

*Naphthalol* (naphthaline), *toluol*, and a considerable number of carbides of hydrogen, behave in a like manner.

In which form is the nitrogen contained in these bodies, as, for instance, in nitrobenzol?

The perfect neutrality of this substance, its ether-like taste and odour, induced some chemists to suppose that its elements might be similarly arranged to those of the compound ethers. Nitrobenzol, according to this view, may be considered as a compound of an organic oxide with nitrous acid, corresponding to nitrous ether.

Nitrite of oxide of ethyl $C_4\ H_5\ O,\ NO_3$, nitrous ether.
Nitrite of oxide of benzide $C_{12}\ H_5\ O,\ NO_3$, nitrobenzol.

These views, which appear at the first glance very reasonable, lose however by a closer examination a considerable portion of their probability. Independent of the fact that oxide of benzid is merely an hypothetical compound while we know the oxide of ethyl in an isolated state, the behaviour of these two bodies towards potassa is sufficient to show a decided dissimilarity in their constitution. Nitrous ether, like all the other compound ethers, is decomposed by potassa, giving rise to nitrite of potassa and alcohol (Liebig). Nitrobenzol, when similarly treated, yields no acid of nitrogen; an aqueous solution of potassa leaves this body quite intact, and when employed in alcoholic solution, the latter is oxidized and *azobenzol* (*azobenzide*), *i. e.* nitrobenzol minus oxygen, is formed*. We see here that all analogy between nitrous ether and nitrobenzol disappears entirely.

Nitrobenzol undergoes still another change, which does not in any way agree with the benzide theory. According to Deville†, this body, when repeatedly treated with fuming nitric acid, yields a crystalline substance, to which he has assigned the name binitrobenzol (binitrobenzide). This body‡, according to the theory in question, was considered to be a compound of 2 equivalents of nitrous acid with a higher oxide of benzide, *i. e.* that its constitution must be according to the formula $C_{12}\ H_5\ O_2, 2NO_3$. That his view is not tenable, without mentioning other objections to it, is evident, inasmuch as the above formula does not express the composition of the new compound; for, according to Deville's analysis, we find that instead of five it only contains four equivalents of hydrogen.

* *Ann. der Chemie und Pharm.*, vol. liii. p. 28.
† *Ann. de Chem. et de Phys.*, 3 ser., t. iii. p. 157.
‡ Berzelius, *Jahresbericht*, 1843.

Recently certain French chemists, Laurent, for example, have represented these bodies under a different aspect. A great number of investigations had led to the conclusion that the hydrogen of many compounds may be wholly or partly replaced by a corresponding number of equivalents of chlorine and bromine without altering the fundamental properties. This law had been established for a number of acids and indifferent bodies, and an investigation published some months since* by one of us has proved that the same law extends also to bodies possessing basic properties, which at first sight appeared improbable.

The same view may be applied to many products which have assumed nitrogen and oxygen from nitric acid. These compounds may indeed be regarded as simple products of substitution, in which the hydrogen, instead of being replaced by chlorine or bromine, is replaced by a compound radical, namely by hyponitric acid. Whilst in the assumption of chlorine into an organic body, the replaced hydrogen is taken up by another equivalent of chlorine, forming hydrochloric acid; in the employment of nitric acid, the fifth equivalent of oxygen combines with the replaced hydrogen, forming water. Benzoic acid, $HO, C_{14} H_5 O_3$, furnishes, when treated with chlorine, an acid,

$$HO, C_{14} \left\{ \begin{matrix} H_4 \\ Cl \end{matrix} \right\} O_3,$$

which can scarcely be distinguished from the original compound.

Moreover, nitrobenzoic acid, which is produced by the action of nitric acid upon benzoic acid, has been in many cases confounded with benzoic acid. The constitution of this acid, according to the theory of substitution, is

$$HO, C_{14} \left\{ \begin{matrix} H_4 \\ NO_4 \end{matrix} \right\} O_8;$$

and it therefore may be regarded as strictly analogous to chlorobenzoic acid.

In a similar way we have chloro-, bromo- and nitro-salicylic acid.

| | |
|---|---|
| Salicylic acid . . . | $HO, C_{14} H_5 O_5$ |
| Chlorosalicylic acid . | $HO, C_{14} \left\{ \begin{matrix} H_4 \\ Cl \end{matrix} \right\} O_5$ |
| Bromosalicylic acid . | $HO, C_{14} \left\{ \begin{matrix} H_4 \\ Br \end{matrix} \right\} O_5$ |
| Nitrosalicylic acid . | $HO, C_{14} \left\{ \begin{matrix} H_4 \\ NO_4 \end{matrix} \right\} O_5.$ |

Carbazotic acid contains not less than 3 equivalents of ni-

* Transactions of the Chemical Society, vol. ii. p. 266.

trogen; now if we suppose the whole of this element to exist in the form of hyponitric acid, its empirical formula, $HO, C_{12} H_2 N_3 O_{13}$, may be theoretically represented by the following:—

$$HO, C_{12}\left\{\begin{matrix} H_2 \\ 3NO_4 \end{matrix}\right\}O,$$

and thus it would be a simple product of substitution of the compound $HO, C_{12} H_5 O$, which was discovered by Runge in coal-gas naphtha, described by him under the designation of carbolic acid, the same body which was subsequently analysed by Laurent, and termed by him hydrate of phenyl. In fact this substance loses under the influence of chlorine, bromine and nitric acid, one equivalent of hydrogen after another, into the place of which a corresponding number of equivalents of the elements or the compound $NO_4$ enter. We obtain in this way a series of products of substitution, the last member of which, on the one side, is chlorophenusic acid, and on the other carbazotic acid.

| | |
|---|---|
| Hydrate of Phenyl<br>Phenol. | $HO, C_{12} H_5 O.$ |
| Bromophenasic acid<br>Bromophenol | $HO, C_{12}\left\{\begin{matrix} H \\ Br \end{matrix}\right\}O.$ |
| Chlorophenesic acid<br>Dichlorophenol | $HO, C_{12}\left\{\begin{matrix} H_3 \\ Cl_2 \end{matrix}\right\}O.$ |
| Chlorophenisic acid<br>Trichlorophenol | $HO, C_{12}\left\{\begin{matrix} H_2 \\ Cl_3 \end{matrix}\right\}O.$ |
| Chlorophenusic acid<br>Pentachlorophenol | $HO, C_{12} Cl_5 O$ |
| Nitrophenesic acid<br>Dinitrophenol | $HO, C_{12}\left\{\begin{matrix} H_3 \\ 2NO_4 \end{matrix}\right\}O.$ |
| Nitrophenisic acid<br>Trinitrophenol<br>Carbazotic acid | $HO, C_{12}\left\{\begin{matrix} H_2 \\ 3NO_4 \end{matrix}\right\}O.$ |

The same view may be taken of the products resulting from the action of nitric acid upon benzol.

Nitrobenzol is simply benzol, in which 1 equivalent of hydrogen is replaced by hyponitric acid, and in dinitrobenzol 2 equivalents of hydrogen are replaced, as the name implies.

| | |
|---|---|
| Benzol . . . | $C_{12} H_6.$ |
| Nitrobenzol . | $C_{12}\left\{\begin{matrix} H_5 \\ NO_4 \end{matrix}\right.$ |
| Dinitrobenzol . | $C_{12}\left\{\begin{matrix} H_4 \\ 2NO_4 \end{matrix}\right.$ |

The chemical character of these three compounds is not essentially different.

As the substitution of chlorine and bromine for the hy-

drogen of organic bodies has only recently been extended to bases, so until now the replacement of hydrogen by hyponitric acid has been limited to acids and neutral bodies; it therefore appeared to be a point of great interest to ascertain whether indeed $NO_4$ also could replace hydrogen in basic compounds without destroying their electro-positive character. There have been, in fact, some investigations made in this direction. Laurent lately discovered a new base among the products of distillation of hydrobenzamide, remarkable for its high atomic weight. This base, which may be obtained in fine crystals, and is by Laurent called lophine, is converted, when boiled with nitric acid, into a yellow crystalline powder, which manifestly must be considered a product of substitution of lophine. Laurent's analysis gives the following composition to this base: $C_{46}H_{16}N_2$, and the yellow powder is represented by

$$C_{46}\left\{\begin{matrix}H_{13}\\3NO_4\end{matrix}\right\}N_2.$$

In this body (nitrolophyl, trinitrolophine), according to the view in question, 3 equivalents of hydrogen are replaced by hyponitric acid; but with this interchange lophine has lost all its basic properties, trinitrolophine being an indifferent substance.

In pursuing this track of investigation, we endeavoured to supply the hiatus existing here by finding a basic compound into which $NO_4$ might enter without affecting its properties. The various ways in which aniline is formed, its characteristic properties, and above all having succeeded in replacing hydrogen by bromine and chlorine in aniline, we deemed this body the best suited to our experiments.

In the first place, we attempted to accomplish our purpose by the direct action of nitric acid on aniline, but we did not in this way succeed: when aniline is mixed with pretty strong nitric acid, a mass of crystals are formed, which are nitrate of aniline. On heating this salt in the presence of free nitric acid it dissolves with violent action and the escape of nitrous fumes, and is, as we know, ultimately converted, on continuing the treatment, into carbazotic acid. Were it possible to obtain nitraniline by this process, it obviously could only be by interrupting the action of nitric acid at the proper time, but after a number of experiments with acid of every variety of strength, and adding water at every stage of the process, we could not succeed; either the aniline separated unchanged, or its molecular constitution underwent an entire change, and the water separated resinous matters rather of an acid than a basic character. We soon abandoned this method, and

remembering that the chlorine and bromine bases were produced only indirectly, we sought to accomplish our present purpose in the same manner.

After the fact had been established, that isatine was converted into aniline by fusion with caustic potassa, the production of the chlorine and bromine bases followed as a matter of course; in the same way, if we could succeed in producing nitrisatine, $C_{16}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right\}NO_4$, by replacing the hydrogen of isatine with hyponitric acid, the distillation of this compound with potassa might yield nitraniline,

$$\underbrace{C_{16}H_5NO_4}_{\text{Isatine.}} + 4(KO, HO) = \underbrace{C_{12}H_7N}_{\text{Aniline.}} + 4(KO, CO_2) + 2H$$

$$\underbrace{C_{16}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right\}NO_4}_{\text{Nitrisatine.}} + 4(KO, HO) = \underbrace{C_{12}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}N}_{\text{Nitraniline.}} + 4(KO, CO_2) + 2H.$$

On studying however the action of nitric acid upon isatine, we soon found that the yellow powder which is formed is not simply a substitution product of isatine, but belongs evidently to one of the families of bodies containing less carbon, which proceed from the indigo series. It was therefore obvious that by distilling this compound with hydrate of potassa, we could not effect our purpose.

A third mode for the preparation of nitraniline occurred to us. One of the manifold sources of aniline is the destructive distillation of anthranilic acid, which simply loses 2 equivalents of carbonic acid; isomeric with this acid is salicylamide, recently described by Cahours*. The composition of these two bodies is represented by the formula $C_{14}H_7NO_4$. Now if the salicylamide underwent the same decomposition by heat as anthranilic acid, it might obviously be supposed that the nitraniline would result from the distillation of nitrosalicylamide, a substance also lately prepared by Cahours.

$$\underbrace{C_{14}H_5O_4NH_2}_{\text{Salicylamide.}} - 2CO_2 = C_{12}H_5NH_2 \text{ or } \underbrace{C_{12}H_7N}_{\text{Aniline.}}$$

$$\underbrace{C_{12}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right\}O_4, NH_2}_{\text{Nitrosalicylamide.}} - 2CO_2 = C_{12}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right\}NH_2 \text{ or } \underbrace{C_{12}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}N}_{\text{Nitraniline.}}.$$

There were some researches made in this direction, the results of which we published at the beginning of last year†.

The exceedingly small amount of aniline, however, which

* *Ann. der Chem. und Pharm.* vol. xl. p. 64.

† Transactions of the Chemical Society, vol. ii. p. 249.

the distillation of salicylamide had yielded (the principal products being hydrate of phenyl and ammonia), could never warrant a similar treatment of nitrosalicylamide, in order to obtain a sufficient quantity of nitraniline for analysis and a complete study of its properties.

There yet remained to us one resource. We have already mentioned a compound which is produced by the continued action of nitric acid upon nitrobenzol, *i. e.* dinitrobenzol,

$$C_{12}\left\{\begin{matrix}H_4\\2NO_4\end{matrix}\right.$$

which we may consider as nitrobenzol, in which a second equivalent of hydrogen is replaced by hyponitric acid. Chemists are well-acquainted with the interesting transformation which nitrobenzol suffers with reducing agents. By assuming hydrogen and eliminating oxygen, it is perfectly converted into *aniline.*

What, we may ask, would be the action of reducing means upon dinitrobenzol? Various changes might be expected. If all the oxygen were eliminated we might form a substance possessing the formula $C_{12}\,H_4\,N_2$; but it was also conceivable that the reduction would extend only to 1 equivalent of hyponitric acid, and that the other equivalent might form part of the new body; in other words, that we might produce nitraniline,

$$C_{12}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}N.$$

We were just about to make the experiment, when some researches of Zinin* were published, on the action of hydrosulphuric acid upon *dinitronaphthalol* (nitronaphthalese) and dinitrobenzol, which appeared very unfavourable to our views.

Zinin found that by the action of hydrosulphuric acid upon dinitronaphthalol, a new base is formed containing no oxygen. By analogy this body should possess the composition—

$$\underbrace{C_{20}\,H_{10}\,N_2}_{\text{New base.}}$$

$$\underbrace{C_{20}\left\{\begin{matrix}H_6\\2NO_4\end{matrix}\right\}}_{\text{Dinitronaphthalol.}} + 12HS = \underbrace{C_{20}\,H_{10}\,N_2}_{\text{New base.}} + 8HO + 12S.$$

But Zinin found, on analysing the double salt of this base with bichloride of platinum, that its equivalent was only half,

$$\frac{C_{20}\,H_{10}\,N_2}{2} = C_{10}\,H_5\,N,$$

* Erdmann's *Journ. für Prakt. Chemie*, vol. xxxiii. p. 29.

showing that a division had taken place, whence he gave the name seminaphthalidine to the new body.

Seminaphthalidine is a well-characterized organic alkaloid, forming with acids fine crystallizable salts. Zinin obtained by the action of hydrosulphuric acid upon dinitrobenzol the same result, but in this case far less decided. A difficultly crystallizable substance is formed, also possessing a basic nature, which however could not be obtained in the state of purity. An approximative analysis of this substance showed it to be analogous to the seminaphthalidine, *i. e.* $C_6 H_4 N$. Zinin himself remarked, that this substance required a closer examination. These researches appeared to cut off all hopes of our ever obtaining nitraniline; nevertheless we considered a continuation of our experiments in every way desirable, so as at least to solve the questions that remained unanswered in Zinin's experiments. By doing so we very soon obtained results which had escaped the observation of Zinin, and which brought us to the point we aimed at.

For our research we had to prepare a large quantity of dinitrobenzol. The transformation of nitrobenzol into dinitrobenzol proceeds very slowly, even when it is boiled repeatedly with the strongest nitric acid. It is obtained however very speedily by dropping benzol or nitrobenzol into a mixture composed of equal parts of fuming nitric acid and concentrated sulphuric acid, as long as the liquid remains homogeneous. The liquid is now boiled for a few minutes and then allowed to cool. A thick mass of dinitrobenzol is formed, which by washing with water is freed from all adhering acid. One recrystallization from alcohol furnishes this body in long, shining, needle-shaped prisms of absolute purity.

A combustion of these crystals gave us the following results:—

0·2978 grm. dinitrobenzol gave 0·4728 grm. carbonic acid and 0·0650 grm. water.

These results afford in 100 parts—

| | |
|---|---|
| Carbon . . . | 43·26 |
| Hydrogen . . | 2·42 |

| | | | | Calculated. | Found. |
|---|---|---|---|---|---|
| 12 | equivs. of | Carbon . . | 900·00 | 42·77 | 43·26 |
| 4 | ... | Hydrogen . | 50·00 | 2·37 | 2·42 |
| 2 | ... | Nitrogen . . | 354·00 | 16·82 | |
| 8 | ... | Oxygen . . | 800·00 | 38·04 | |
| | | | 2104·00 | 100·00 | |

*Preparation of Nitraniline.*

When an alcoholic solution of dinitrobenzol is saturated

with ammoniacal gas it assumes a dark red colour, and by then passing a stream of hydrosulphuric acid gas through this solution, a large quantity of crystals of sulphur are deposited. By continuing to pass hydrosulphuric acid gas through the solution until only a small quantity of sulphur precipitates, it will contain very little undecomposed dinitrobenzol. By adding hydrochloric acid to this solution and boiling, a new portion of sulphur, mixed with a trace of dinitrobenzol, is thrown down. The whole is now filtered, and to the filtrate potassa is added, a brown matter separates, which unites and settles in a resinous mass at the bottom of the vessel. We washed this matter with cold water until all the alkali was removed. It dissolved completely in alcohol and ether, imparting to them a reddish-brown colour; hot water dissolved the greater part of it, but even after continued boiling in this solvent small quantities of a brown resin remained undissolved. The hot aqueous solution possessed a fine orange-yellow colour; upon cooling it afforded beautiful yellow crystals about an inch in length, which, when recrystallized from water, were perfectly pure.

### *Composition of Nitraniline.*

The crystalline matter prepared in the process described, possesses all the properties of a true organic base, obviously quite dissimilar to that obtained by Zinin. The physical properties of the two bodies could scarcely be more unlike. Elementary analysis proved immediately the difference of the two substances, and showed that the crystals, in fact, belonged to the body which we had endeavoured to procure in such a variety of ways.

By a combustion of the yellow crystals with oxide of copper the following results were obtained:—

I. 0·3035 grm. of substance gave 0·5865 grm. of carbonic acid and 0·1275 grm. of water.

II. 0·3748 grm. substance gave 0·7119 grm. carbonic acid and 0·1493 grm. water.

III. The nitrogen was determined by Dumas's method in an atmosphere of carbonic acid.

*Results.*—0·4260 grm. of substance gave 80 cubic centimetres of moist nitrogen. Barometer 324‴, Thermometer 16° centig.

These numerical results represent the following per cents.

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . | 52·70 | 51·80 | |
| Hydrogen . | 4·66 | 4·42 | |
| Nitrogen . . | ... | ... | 20·52 |

agreeing exactly with the formula of nitraniline,

$$C_{12}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}N.$$

The mean of our analysis, compared with the calculated numbers, stands as follows:—

| | | Theory. | | Mean of the exp. |
|---|---|---|---|---|
| 12 equivs. | Carbon | 900·00 | 52·05 | 52·25 |
| 6 ... | Hydrogen | 75·00 | 4·33 | 4·54 |
| 2 ... | Nitrogen | 354·00 | 20·47 | 20·52 |
| 4 ... | Oxygen | 400·00 | 23·14 | |
| | | 1729·00 | 100·00 | |

In order to control this formula, we prepared the double compound of the new base with bichloride of platinum. On igniting this salt 0·5240 grm. gave 0·1500 grm. = 28·62 per cent. of platinum.

Atomic weight from experiment . . 1739·5
Atomic weight, theoretical . . . . 1729·0.

The metamorphosis of dinitrobenzol under the influence of reducing agents is thus perfectly analogous to the transformation of nitrobenzol. In fact the decomposition is very simple, if we regard dinitrobenzol as nitrobenzol, in which one equivalent of hydrogen is replaced by hyponitric acid.

$$\underbrace{C_{12}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right\}NO_4}_{\text{Dinitrobenzol.}}+6\,HS=\underbrace{C_{12}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}N}_{\text{Nitraniline.}}+4HO+6S$$

*Properties of Nitraniline.*

Nitraniline, as we have stated, is obtained from a hot aqueous solution, in the form of long yellow crystals. It is very sparingly soluble in cold water, so that nearly the whole is separated by crystallizing from this solvent. Alcohol and ether also dissolve this base; from the former it crystallizes in silky needles, and from the latter in the same form, but not so well defined. Nitraniline dissolves in all acids, from which potassa separates it in yellow flakes, which under the microscope have a confused, needle-like structure. At the ordinary temperature the base possesses no odour, but when slightly warmed, it evolves a peculiar aromatic odour, which somewhat resembles aniline. Its taste is burning. When the crystals are heated they melt into a deep yellow oil, which passes into a yellowish vapour, condensing in beautiful iridescent plates upon the cold interior surface of the vessel. Nitraniline sublimes without fusing when heated in a water-

bath, yielding a sublimate of most beautiful crystals. At a higher temperature the base distils, leaving no residue, and the liquid which passes over solidifies in the receiver or in the neck of the retort into a scaly mass. The boiling-point of the base lies higher than 285° C. (545° Fahr.), and the fusing-point at about 110° C. (230° Fahr.). Its vapour burns with a smoky flame.

Nitraniline is specifically heavier than water; it affords not the slightest reaction with test papers; even rose paper, which is so exceedingly sensitive for alkalies, is not at all affected by it. The properties of nitraniline agree in many respects with those of aniline, chlor- and bromaniline. Like these bases it possesses in a high degree the property of imparting an intense yellow colour to fir-wood. This base also stains the skin in no less degree than carbazotic acid, nitrophenesic acid, &c.; but it does not afford the beautiful reaction with hypochlorite of lime which characterizes aniline.

Nitraniline displaces none of the metallic oxides from their acid compounds; its basic properties are exceedingly weak. Aniline displaces this base from all its salts.

### *Compounds of Nitraniline.*

Although nitraniline is so weak a base, it combines with acids, affording crystallizable salts, which possess the same constitution as the corresponding salts of aniline. All its salts are decidedly acid to test papers. They are decomposed by the caustic and carbonated alkalies, nitraniline separating in a crystalline form. We have investigated the subjoined salts in order to be completely satisfied with respect to the composition and nature of the base.

*Hydrochlorate of Nitraniline*, $C_{12}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}N$, HCl.—It is obtained by evaporating a solution of nitraniline in hydrochloric acid. The colour of nitraniline entirely disappears in this solvent, and fine scales are obtained, shining like mother-of-pearl. This salt is extremely soluble in water and alcohol.

*Analysis.*—0·4055 grm. of salt gave 0·3350 grm. chloride of silver, or 20·37 per cent of chlorine.

| | | | Theory. | Found. |
|---|---|---|---|---|
| 12 equivs. | Carbon . . | 900·00 | 41·23 | |
| 7 ... | Hydrogen . | 87·50 | 4·00 | |
| 2 ... | Nitrogen . | 354·00 | 16·22 | |
| 4 ... | Oxygen . . | 400·00 | 18·32 | |
| 1 ... | Chlorine . | 442·65 | 20·23 | 20·37 |
| | | 2184·15 | 100·00 | |

*Binoxalate of Nitraniline*, $C_{12}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}N, HO, 2(C_2O_3, HO)$. —This salt is obtained on mixing a solution of nitraniline in alcohol with oxalic acid dissolved in the same solvent. This salt separates in the form of yellowish crystals, which are washed with ether and dried upon a porous tile.

The combustion of this compound with chromate of lead afforded the following numbers:—

0·4985 grm. of salt gave 0·7550 grm. carbonic acid and 0·1790 grm. water. In 100 parts—

| | | |
|---|---|---|
| Carbon . . . . | 41·30 | |
| Hydrogen . . . | 3·99 | |

| | | | Theory. | Found. |
|---|---|---|---|---|
| 16 equivs. | Carbon . . | 1200·00 | 40·45 | 41·30 |
| 9 ... | Hydrogen . | 112·50 | 3·79 | 3·99 |
| 2 ... | Nitrogen . | 354·00 | 11·93 | |
| 13 ... | Oxygen . . | 1300·00 | 43·83 | |
| | | 2966·50 | 100·00 | |

The above numbers show the slight excess of carbon which often occurs with the substitution products of hyponitric acid, especially when the combustion is carried on rather quickly. Unfortunately we had no more of the base to prepare this salt again, but there is little doubt but that the analysed salt corresponds with the binoxalate of chloraniline*.

*Double Salt of Hydrochlorate of Nitraniline and Bichloride of Platinum*, $C_{12}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}N, HCl, Pt\,Cl_2$.—An aqueous solution of hydrochlorate of nitraniline is not precipitated by deutochloride of platinum; but when an alcoholic solution of the former is mixed with the latter, a yellow crystalline double salt is formed, which is exceedingly soluble in both water and alcohol, and therefore must be washed with ether. We have already alluded to the determination of the platinum in this salt when treating of the atomic weight of the base. We append the calculated composition of this salt along with the platinum per-centage found.

| | | | Theory. | Found. |
|---|---|---|---|---|
| 12 equivs. | Carbon . . | 900·00 | 20·91 | |
| 7 ... | Hydrogen . | 87·50 | 2·03 | |
| 2 ... | Nitrogen . | 354·00 | 8·23 | |
| 4 ... | Oxygen . . | 400·00 | 9·30 | |
| 3 ... | Chlorine . | 1327·95 | 30·87 | |
| 1 ... | Platinum . | 1233·50 | 28·66 | 28·62 |
| | | 4302·95 | 100·00 | |

We have not examined the other salts of nitraniline.

* Transactions of the Chemical Society, vol. ii. p. 227.

*Products of the Decomposition of Nitraniline.*

We have not as yet made many experiments in this direction, owing to the great difficulty of obtaining the base in sufficient quantity; we can therefore only give a few reactions.

Nitric acid violently decomposes nitraniline, and after continued boiling affords an acid which we have not more closely examined. There is little doubt but that it is carbazotic acid.

When this base is treated with bromine violent action takes place, accompanied by an elevation of temperature and a strong disengagement of hydrobromic acid. After some time the whole is changed into a brown resinous mass, which crystallizes from alcohol in the form of yellowish needles. This body is insoluble in water and perfectly neutral, combining neither with acids nor alkalies. It is manifestly nitrodibromaniline, corresponding with tribromaniline. We may regard the following as the formula, although as yet we have not analysed the substance:—

$$C_{12}\left\{\begin{matrix}H_4\\NO_4\\Br_2\end{matrix}\right\}N-(?)$$

The production of nitraniline appears to us to be interesting, in reference to the question of substitution, which is still in debate amongst chemists. If we reject that theory, we can scarcely understand the constitution of this base and its relations to aniline.

The group of aniline compounds has thus been again augmented by the discovery of nitraniline. The following is a synopsis of the different members of this family:—

| | |
|---|---|
| Aniline . . . . . | $C_{12}\,H_7\,N.$ |
| Chloraniline . . . . | $C_{12}\left\{\begin{matrix}H_6\\Cl\end{matrix}\right\}N.$ |
| Dichloraniline . . . | $C_{12}\left\{\begin{matrix}H_5\\Cl_2\end{matrix}\right\}N.$ |
| Trichloraniline . . . | $C_{12}\left\{\begin{matrix}H_4\\Cl_3\end{matrix}\right\}N.$ |
| Chlorodibromaniline . | $C_{12}\left\{\begin{matrix}H_4\\Cl\\Br_2\end{matrix}\right\}N.$ |
| Bromaniline . . . . | $C_{12}\left\{\begin{matrix}H_6\\Br\end{matrix}\right\}N.$ |
| Dibromaniline . . . | $C_{12}\left\{\begin{matrix}H_5\\Br_2\end{matrix}\right\}N.$ |
| Tribromaniline . . . | $C_{12}\left\{\begin{matrix}H_4\\Br_3\end{matrix}\right\}N.$ |

Nitraniline . . . . . $C_{12}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}N.$

Nitrodibromaniline . . $C_{12}\left\{\begin{matrix}H_4\\NO_4\\Br_2\end{matrix}\right\}N.$ (?)

In concluding this memoir, we may remark that the body which Zinin obtained by treating dinitrobenzol in the same manner, *i. e.* the compound $C_6 H_4 N$, is evidently the last product of the action of the hydrosulphuric acid upon dinitrobenzol, our nitraniline being the first. Zinin's compound will doubtless be procured by the further action of reducing agents upon nitraniline. We shall shortly ascertain this.

$$\underbrace{C_{12}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}N}_{\text{Nitraniline.}} + 6HS = \underbrace{2C_6 H_4 N}_{\text{Semianiline.}} + 4HO + 6S.$$

The small quantity of resinous matter which remains behind upon dissolving crude nitraniline in boiling water is probably Zinin's semianiline.

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## CLXV. *On the Blue Compounds of Cyanogen and Iron.* By Alexander W. Williamson, *Esq.*, *Ph.D.*

IT is a well-known fact that the different substances which pass by the general name of prussian blue, when prepared in the usual way, are not pure combinations of iron, but invariably contain potassium, of which the quantity varies according to the circumstances under which they are formed. It has been the subject of frequent experiment to decide whether this potassium should be considered as an admixture or as an essential constituent, and in the latter case to discover what part it plays in the constitution of the compound. Among those various researches we may confine ourselves to the consideration of those of Berzelius* and Gay-Lussac†.

Gay-Lussac found that prussian blue retains potassium so tenaciously that the latter cannot by mere washing be removed from it; for as soon as the precipitate had been freed from all potassium, it was found to consist no longer of prussian blue, but hydrated oxide of iron. From this fact he concludes that the purest prussian blue contains potassium. Berzelius, on the contrary, by washing continuously for three weeks a precipitate of ferrocyanide of potassium with a persalt

* Poggendorff's *Annalen*, vol. xxi. p. 490.

† Ibid. vol. xxv. p. 385.

of iron, succeeded in obtaining a substance, which, though retaining the colour of the original compound, was perfectly free from potassium. The water passing through in the later periods of the operation contained this potassium in the form of ferridcyanide, the formation of which salt he attributes to a process of oxidation resulting from the action of the air; thus admitting that a decomposition of the original precipitate accompanied the removal of the potassium. Without the proof afforded by an analysis, or some characteristic reaction, we cannot venture to conclude that the residue after this decomposing reaction retained the composition of prussian blue. Berzelius thus agrees with Gay-Lussac in the fact that a decomposition of the prussian blue is a necessary condition for the removal of the potassium. The difference consisted only in the kind of decomposition which took place: in Berzelius's experiments the residue after decomposition still maintained a blue colour, while in Gay-Lussac's, in which by the action of a water which he himself concluded must have been alkaline, the residue consisted of peroxide of iron. Both lead however to the same conclusion.

Berzelius analysed two kinds of prussian blue containing potassium. The first, which was soluble in water, he found, after separation by means of alcohol from the red and yellow cyanides, which were simultaneously formed, to contain for every 12 atoms of iron 1 of potassium. The other, which was insoluble in water as it remained on the filter, from which the soluble salt had been washed away, contained iron and potassium in the proportion of 8 equivalents to 1. The former of these substances he considers as a combination of 2 atoms of the yellow prussiate with 3 atoms of prussian blue,—

$$2(Fe\ K_2\ Cy_3) + 3(Fe_7\ Cy_9).$$

The second is a combination of 1 atom yellow prussiate with 2 prussian blue,—

$$Fe\ K_2\ Cy_3 + 2(Fe_7\ Cy_9).$$

This great chemist admits however, what indeed the complex nature of these formulæ sufficiently indicates, that further light is needed on the nature of these compounds than these analyses afford.

I shall now describe the results of some experiments which I have performed in the laboratory of Professor Liebig, for the purpose of gaining some further insight into the composition and nature of these salts, and of deciding the question of the existence of the pure compounds of iron of which the formulæ have been given on purely theoretical grounds.

It is well known that when ferrocyanide of potassium is

boiled with dilute sulphuric acid, only a part of the cyanogen is given off as hydrocyanic acid, and that a greenish substance remains behind containing all the iron and a considerable quantity of the potassium in combination with cyanogen; also that this substance by exposure to the air gradually changes into a deep blue. This process is much favoured, as Gay-Lussac observed, by the presence of free acid, and is accompanied by the formation of a potassium salt of this acid. This green substance consists, according to the analysis of Everitt, which M. Geiger repeated in this laboratory, of 3 equivalents cyanogen, 2 iron and 1 potassium. My analysis confirms this composition. 2·372 grammes ferrocyanide of potassium were distilled with water, and sulphuric acid equivalent to the quantity of potassium in the salt, and the distillation was continued until no more prussic acid passed over. The residue, after this treatment, was washed out on a filter, air being excluded, dried and cautiously heated in a platinum crucible with concentrated sulphuric acid, which decomposed all the cyanogen and converted the iron and potassium into sulphates. The aqueous solution of these salts was decomposed by ammonia, filtered, evaporated and heated to redness. 0·532 gramme sulphate of potash was thus obtained, which corresponds to 10·08 per cent. of potassium instead of 10·67 per cent., which the above formula requires.

The compound may be considered as ferrocyanide of potassium, in which 1 atom of potassium is replaced by iron, and may be expressed by the following formula:—

$$\mathrm{Cfy}\left\{\begin{matrix}\mathrm{Fe}\\ \mathrm{K}\end{matrix}\right.$$

Its reactions are also such as we must expect from such a compound, for by treating it with caustic potash, a solution of pure ferrocyanide of potassium is formed whilst protoxide of iron is set free. It will be designated in the following lines, ferrocyanide of iron and potassium. The blue compound into which this salt is changed by oxidation has been incorrectly considered as prussian blue. It, however, differs materially in its composition from that body, as I will proceed to show. Its formation takes place very easily, for it is caused by every reagent, such as chlorine, nitric acid, sulphuric acid, with oxygen, &c., which eliminates potash from the white salt. For its preparation, dilute nitric acid, which consists of 1 volume concentrated acid and 20 of water, may be used with most advantage. This liquid, in which the white salt, prepared as above described, is suspended, is heated in an open basin, during which the liquid is frequently stirred. At a low temperature no apparent action ensues; but when the liquid has

nearly reached the boiling-point, an evolution of nitric oxide commences, which gradually increases in briskness, and is accompanied by a speedy change of the white colour to dark blue. As soon as this action has commenced, the basin must be removed from the fire to prevent too violent an action, which would cause the admixture of another substance. If the correct proportion of white salt to acid has been used, the action continues without further heating until the transformation into the blue compound is complete. If, however, the colour should indicate that some of the white salt remains, a small quantity more acid must be added, and the mixture, if necessary, again heated. In order to proceed with certainty, a small portion of the blue substance should be decomposed with potash; should the peroxide of iron which is thus set free contain protoxide, the treatment with nitric acid must be continued; the presence of ferridcyanide of potassium in the solution indicates, on the contrary, that the action has gone too far, in which case the operation must be recommenced with a fresh portion. In this manner a body of a beautiful violet blue colour is formed, containing less potassium than the preceding one. The liquid contains nitrate of potash, but no trace of iron. The substance prepared in this way was thrown on a filter and washed out until the washings left no residue on polished platinum. The compound was not in the least degree affected by this treatment. It retained its original colour, and contained no peroxide of iron soluble in muriatic acid. After being carefully dried at 100° C., it was analysed in the manner which I shall now proceed to describe.

The cyanogen was completely oxidated by a gradually increasing heat applied to it in an open flat-bottomed porcelain crucible. It was thus converted into a mixture of peroxide of iron and carbonate of potash, from which the alkali was extracted by repeatedly boiling with water, and determined as chloride. The residue was determined as peroxide of iron. The cyanogen was determined indirectly by suspending a weighed quantity of the compound in water and decomposing it with potash. The peroxide of iron thus separated necessarily corresponded to the quantity of percyanide, as all protocyanide remained in solution in the form of yellow prussiate.

I. 3·417 grms. gave 0·694 chloride of potassium and 1·630 peroxide of iron, corresponding to 10·6 per cent. potassium and 32·4 per cent. iron.

II. 4·225 grms. gave 0·871 chloride of potassium and 1·986 peroxide of iron, corresponding to 10·87 per cent. potassium and 32·5 per cent. iron.

*Determination of Cyanogen.*

I. 3·744 grms. gave 0·940 peroxide of iron, corresponding to 17·4 per cent. iron as cyanide.

II. 6·125 grms. gave 1·585 peroxide of iron, corresponding to 17·9 per cent. iron as cyanide.

The formula $Fe_4 Cy_6 K + 4Aq$ requires—

| | | I. | II. |
|---|---|---|---|
| $Fe_4$ | 108·8 = 32·0 | 32·4 | 32·5 |
| K | 39·2 = 11·5 | 10·6 | 10·9 |

precipitated by potash—

| | | | |
|---|---|---|---|
| $Fe_2$ | 54·4 = 16·28 | 17·4 | 17·9. |

The deficiency of potassium and corresponding excess of iron are sufficiently accounted for by the imperfect separation by water. The excess of peroxide of iron, corresponding to the cyanide, was caused by its containing some of the potash employed in its separation. In order, however, to remove all doubt of the correctness of the formulæ deduced from these numbers, several combustions with chromate of lead were performed with the greatest accuracy. These are as follows:—

I. 0·427 grm. gave 0·331 $CO_2$ and 0·046 water, corresponding to 21·14 per cent. carbon and 10·78 water.

II. 0·320 grm. gave 0·247 $CO_2$ and 0·036 water, corresponding to 21·05 per cent. carbon and 11·15 water.

III. 0·721 grm. gave 0·559 $CO_2$ and 0·081 water, corresponding to 21·14 per cent. carbon and 11·3 water.

| | Calculated. | I. | II. | III. |
|---|---|---|---|---|
| $C_{12}$ . . 72 | 21·17 | 21·14 | 21·05 | 21·14 |
| 4Aq . 36 | 10·59 | 10·78 | 11·15 | 11·3 |

The approximation here is sufficient.

This compound is particularly remarkable for its brilliant violet-blue colour. In a finely divided state, as is obtained by suspension in a large quantity of water, it is transparent with a green colour. It does not possess when dry the coppery lustre so characteristic of prussian blue. It may be viewed as ferridcyanide of potassium, in which 2 atoms of potassium are replaced by iron, and it bears the same relation to the above-described white compound, $Cfy\left\{\begin{matrix}Fe\\K\end{matrix}\right.$, as Gmelin's salt to the yellow prussiate. The manner of its formation is also the same, for 2 atoms ferrocyanide of iron and potassium unite, giving up 1 atom of potassium, just as in the case of yellow prussiate.

$$2\left(Cfy\left\{\begin{matrix}Fe\\K\end{matrix}\right.\right) + Cl = 2Cfy\left\{\begin{matrix}2Fe\\K\end{matrix}\right. + KCl.$$

We may call it, according to the customary nomenclature,

ferridcyanide of iron and potassium. It has been mentioned above, that on treating it with potash, ferrocyanide of potassium is formed, and hydrated oxide of iron is set free. It is evident that in this reaction 2 atoms of iron are replaced by 3 of potassium, whilst the oxygen of the potash combines with the iron.

On heating this blue compound with a solution of yellow prussiate it changes it into ferridcyanide; if the blue compound be in excess no trace of yellow prussiate remains behind. 3·473 grms. ferridcyanide of iron and potassium were suspended in an excess of ferrocyanide, and digested with it for a considerable time. Collected on a filter, it was of a pale blue colour and gave 1·39 grm. sulphate of potash, corresponding to 0·624 potassium, of which, before the treatment with ferrocyanide, it only contained 0·411. Hence it is evident that the reaction consists in potassium being taken from the yellow prussiate, and half of the ferridcyanide of iron and potassium changed into ferrocyanide. This reaction may even be applied with advantage to the preparation of larger quantities of pure red prussiate, for it presents neither of the disadvantages attending the decomposition by chlorine, viz. the admixture of chloride of potassium, which is unfavourable to crystallization, and also the well-known green substance, which is formed by the slightest excess of chlorine. The blue salt may of course be used repeatedly for this operation, as it is immediately restored by warming with nitric acid.

By long-continued boiling with nitric acid, this blue compound is changed into a rich dark green, which contains a greater proportion of cyanogen and a small quantity of potassium. It is reduced by the action of light, which gradually changes its colour to a blue. For analysis, it was heated with concentrated sulphuric acid until all cyanogen was destroyed; the iron and potassium were determined as peroxide and sulphate of potash.

I. 2·966 grms. gave 1·527 peroxide of iron and 0·147 sulphate of potash, corresponding to 35·72 per cent. iron and 2·23 per cent. potassium.

II. 3·172 grms. gave 1·637 peroxide of iron and 0·159 sulphate of potash, corresponding to 35·97 per cent. iron and 2·25 per cent. potassium.

Burned with chromate of lead it gave the following numbers:—

I. 0·421 grm. gave 0·361 carbonic acid and 0·058 water, corresponding to 23·3 per cent. carbon and 13·6 water.

II. 0·151 grm. gave 0·121 carbonic acid and 0·020 water, corresponding to 23·2 per cent. carbon and 13·3 water.

This quantity of potassium is too small to justify the conclusion that it is essential to the composition of the salt, as it only amounts to about 1 equiv. to 24 iron. Its equivalent of iron was therefore added to the other iron, and in this manner numbers found which correspond to the formula $Cy_7\ Fe_5 + 5$ aq, as is shown by the following:—

| | Calculated. | Found. I. | II. |
|---|---|---|---|
| $C_{14}$ | 84 = 23·14 | 23·3 | 23·2 |
| $Fe_5$ | 136 = 37·5 | 37·17 | 37·27 |
| $Aq_5$ | 45 = 12·4 | 13·6 | 13·3 |

On treating this body with potash, peroxide of iron is separated and a brownish-red liquid formed, in which proto- and persalts of iron give a blue precipitate. This liquid is decomposed by boiling, peroxide of iron is precipitated, and the colour of the precipitate becomes much lighter. I am not aware, however, what is the nature of the decomposition. The brown-red colour of the liquid has much similarity with that obtained by mixing ferridcyanide of potassium with a persalt of iron. The green substance which Pelouze obtained by decomposing yellow prussiate by chlorine, and for which he gives the empirical formula $Fe_3\ Cy_4$, is decomposed in a similar manner by potash. If, in accordance with the view of many chemists, we consider this substance analogous to magnetic iron ore, as $Fe_2\ Cy_3 + Fe\ Cy$, the compound which I have described may be viewed as containing a double quantity of percyanide, $2(Fe_2\ Cy_3) + Fe\ Cy$. I will not however venture to express any opinion as to the propriety of considering it as a peculiar compound or not.

It is well known that for technical purposes an esteemed blue colour, which is sometimes called Turnbull's blue, is prepared by decomposing ferridcyanide of potassium with a protosalt of iron. In this compound, which by its colour may be easily distinguished from prussian blue, the presence of potassium has been discovered, but without bringing to light any connection with the composition of the body. It appeared to me not devoid of interest to examine the properties of this substance and subject it to analysis. To a dilute aqueous solution of ferridcyanide of potassium, which had been purified by frequent crystallizations, was added a solution of sulphate of iron, the red salt remaining in excess. In washing out this precipitate I proceeded with particular care, as, whilst removing all substances mixed with the compound, it was necessary to avoid any action upon it which might render soluble any constituents of the salt, as was the case with Berzelius's washing in the air. This object I completely succeeded in attaining, simply by means

of washing with distilled water in a vessel from which air was excluded. The precipitation had been performed in a tall glass cylinder, which was completely filled by the liquids, and could be perfectly closed by a glass plate adjusted to its ground edge. In this vessel the precipitate was washed by subsidence and decantation, during the first period of which the water ran off colourless, or only slightly coloured by the remaining quantity of red prussiate. As soon, however, as the greater part of the soluble salts had been washed away, the liquid no longer deposited all the blue compound suspended in it, but even after standing several hours ran off with a blue colour. In the supposition that I had here a solution of prussian blue, I threw it upon a filter and found that it ran through unchanged. Unwilling however, upon the simple testimony of this fact, to conclude that it was a solution, I transferred it to a filtering apparatus, so contrived that by means of a hydrostatic pressure, which could be varied at pleasure, it was driven through a layer of sixfold filtering paper supported by a linen cloth. This experiment proved that the blue compound was indeed not in solution, but merely in a state of suspension, so fine as to pass through the pores of a simple filter, for it was completely separated by the denser mass of the compressed folds of paper, and a colourless liquid passed through. The washing was continued until the water filtered through in this manner left no visible residue on evaporation on polished platinum. Subsequent experiments showed that this operation may, without affecting the result, be performed more quickly and easily by the use of hot water, as in this case the precipitate assumes a denser form and deposits more easily from the liquid.

I. 1·706 grm. of this substance gave 0·828 peroxide of iron and 0·189 sulphate of potash, corresponding to 33·6 per cent. of iron and 4·96 per cent. of potassium.

II. 1·870 grm. gave 0·909 peroxide of iron and 0·221 sulphate of potash, corresponding to 33·7 per cent. of iron and 5·3 per cent. potassium.

The average of these numbers, namely 33·6 iron and 5·1 potassium, are in the proportion of 9·3 equivalents iron to 1 potassium. It will be shown later how these numbers are to be considered; we see in the meanwhile that they indicate a different composition from that of ferridcyanide of iron and potassium.

I next endeavoured to precipitate in such a manner as if possible to replace all the potassium of Gmelin's salt by iron, which was done by forming the precipitate in an excess of protochloride of iron, and digesting it for several hours with that salt. The substance thus prepared was washed out in

the manner described in the preceding instance, and was found, though not absolutely free from potassium, to contain so extremely small a quantity of this element, as to render a determination of it next to impossible; so that the difference produced by neglecting it fell far within the limit of the ordinary limit of analysis. After drying at the ordinary temperature over sulphuric acid it was subjected to analysis.

I. 0·765 grm. gave 0·383 peroxide of iron, corresponding to 34·6 per cent. of iron.

II. 0·763 grm. gave 0·379 peroxide of iron, corresponding to 34·4 per cent. of iron.

Burnt with chromate of lead,—

I. 0·535 grm. gave 0·344 carbonic acid and 0·155 water, corresponding to 17·5 per cent. carbon and 28·9 water.

II. 0·563 grm. gave 0·359 carbonic acid and 0·157 water, corresponding to 17·4 per cent. carbon and 27·9 water.

III. 0·477 grm. gave 0·307 carbonic acid and 0·135 water, corresponding to 17·5 per cent. carbon and 28·2 water.

The proportion of 5 equivalents of iron to 6 of cyanogen requires to 34·5 of iron, which is the average found, 18·2 carbon instead of 17·5, as is found. If it be considered that the error of iron and carbon determinations are here added together, the accordance will I think be held to be sufficient. My reason for not calculating any formula for the water was, that owing to the readiness with which the compound is decomposed, I was compelled to analyse it without drying at an elevated temperature, which would have produced an evolution of hydrocyanic acid. On decomposing this substance in the fresh prepared state by potash, proto- and peroxides of iron are set free and ferrocyanide of potassium formed. A portion of this compound was, after carefully washing out and without drying, decomposed by carbonate of potash. The proto- and peroxides of iron, thus separated, after long-continued heating in the air, weighed 1·627 grm. of peroxide. The liquid boiled in and treated with sulphuric acid gave 1·077 grm. peroxide of iron. The proportion of 3 to 2 requires 1·623 and 1·082. Of 5 equivalents of iron 3 were separated in combination with 4 atoms of oxygen of the potassium, which takes their place, while the other two being contained in the composition of the radical remained in solution.

I will now pass to the consideration of the manner in which we may consider these elements to be combined. It is well known that ferridcyanide of potassium is reduced by the action of sulphuretted hydrogen, that is to say, it takes up hydrogen, and is thus converted into a mixture of 3 atoms ferrocyanide of potassium and 1 atom hydroferrocyanic acid (or ferrocyanide of hydrogen).

$$\left.\begin{matrix}4\text{Cfy}\ 6\text{K}\\ 2\text{HS}\end{matrix}\right\} = \left\{\begin{matrix}3\text{Cfy}\ 2\text{K}\\ \text{Cfy}\ 2\text{H}\\ 2\text{S}\end{matrix}\right.$$

The fact of the red cyanide being thus reducible is however a property which may in the above instance exercise a considerable influence on the composition of the product, as is shown by the following instructive experiment of Liebig. To a boiling solution of ferridcyancide of potassium was added a small quantity of protosulphate of iron, which was not nearly sufficient to decompose all the cyanide. Ferrocyanide of potassium, which remained in solution, and precipitate of prussian blue (3Cfy 4Fe), were formed:—

$$\left.\begin{matrix}4\text{Cfy}\ 6\text{K}\\ 4\text{FeO}\end{matrix}\right\} = \left\{\begin{matrix}3\text{Cfy}\ 4\text{Fe}\\ \text{Cfy}\ 2\text{K}\\ 4\text{KO}\end{matrix}\right.$$

This reaction leads to a new way of considering the above analysed compound, which is adapted to its composition when containing and also when free from potassium, for if one atom more of protosalt of iron be added than assumed in the above formula of decomposition, it forms, by decomposition with the yellow prussiate, ferrocyanide of iron and potassium, which divided in the already-formed prussian blue, produces a mixture containing iron and potassium in the proportion found by analysis:—

$$\left.\begin{matrix}4\text{Cfy}\ 6\text{K}\\ 5\text{FeO}\end{matrix}\right\} = \left\{\begin{matrix}3\text{Cfy}\ 4\text{Fe}\\ \text{Cfy}\left\{\begin{matrix}\text{Fe}\\ \text{K}\end{matrix}\right.\\ 5\text{KO}\end{matrix}\right.$$

On adding an excess of iron salt the second equivalent of potassium is also replaced by iron, and a mixture of prussian blue and ferrocyanide of iron formed, which contains cyanogen and iron in the proportion of 6 to 5, as found. This view rests upon the supposition that prussian blue (3Cfy 4Fe) is always formed by the decomposition at the ordinary temperature, as was found to be the case at the boiling-point. In the contrary case we must assume that the potassium of the red cyanide is simply replaced by iron:—

$$2\text{Cfy}\ 3\text{K} + 3\text{FeCl} = 2\text{Cfy}\ 3\text{Fe} + 3\text{KCl}$$

$$4\text{Cfy}\ 6\text{K} + 5\text{FeCl} = 4\text{Cfy}\left\{\begin{matrix}5\text{Fe}\\ \text{K}\end{matrix}\right. + 5\text{KCl}$$

In the first case we have ferridcyanide of iron, in the second a double salt of the same with ferridcyanide of iron and potassium.

The separation of $Fe_3O_4$ by potash seems to speak in favour of the view that the precipitate is a mixture of prussian blue and ferrocyanide of iron, as these substances would give this reaction; for if the compound were a ferridcyanide of iron, it would be expected that potash would set free protoxide of

iron and reproduce the red cyanide. It might indeed be replied to this that the red cyanide is reduced by the protoxide in proportion as it is set free:—

$$\left.\begin{matrix}2\mathrm{Cfy}\,3\mathrm{K}\\ \mathrm{KO}\end{matrix}\right\} + 3\mathrm{FeO} = 2(\mathrm{Cfy}\,2\mathrm{K}) + \mathrm{Fe_3O_4}.$$

I described above an experiment of Liebig, showing that by the action of protoxide of iron the red prussiate is reduced to the yellow, but I find that the reverse process takes place with equal facility, that is, the peroxide of iron decomposes the yellow cyanide, forming the red one. A small quantity of perchloride of iron was added to a boiling solution of ferrocyanide of potassium, and the mixture heated for some minutes. The liquid filtered off clear gave a deep blue precipitate with protosulphate of iron:—

$$\left.\begin{matrix}3(\mathrm{Cfy}\,2\mathrm{K})\\ \mathrm{Fe_2O_3}\end{matrix}\right\} = \left\{\begin{matrix}2\mathrm{Cfy}\,3\mathrm{K}\\ \mathrm{Cfy}\,2\mathrm{Fe}\end{matrix}\right\} + 3\mathrm{KO}.$$

I have now endeavoured, as far as possible, to state the two ways of considering these compounds, and will leave the decision to more competent judges.

I next endeavoured to apply the method which had proved so serviceable in obtaining Turnbull's blue free from potassium, viz. digesting the precipitate with an excess of the iron salt, to the preparation of prussian blue of equal purity. A weak solution of yellow prussiate was poured into a great excess of perchloride of iron, and the mixture allowed to stand for some hours exposed to a gentle heat. This precipitate, after being completely washed in the usual manner, gave, on analysis, to 0·707 peroxide of iron, 0·057 sulphate of potash, which numbers are in the proportion of 27 iron to 1 potassium. If this were to be considered as a peculiar compound, it must be,—

$$3(3\mathrm{Cfy}\,4\mathrm{Fe}) + 3\mathrm{Cfy}\left\{\begin{matrix}3\mathrm{Fe}\\ \mathrm{K}\end{matrix}\right.$$

All my endeavours to obtain a precipitate free from potassium were unavailing, as long as this element was present at the formation; I had therefore at last no alternative left but that of precipitating by pure hydroferrocyanic acid. This acid was prepared by mixing a solution of yellow prussiate, from which, by boiling, all atmospheric air had been expelled, with about an equal volume of muriatic acid which had been similarly freed from air, and precipitating by æther. After it had been filtered off and washed with æther, the acid only needed to be dissolved in absolute alcohol and again precipitated by æther to be obtained perfectly pure. It was then dried, dissolved in water, and precipitated with an excess of perchloride of iron. The precipitate thus formed may be distinguished

from common prussian blue by its darker colour. It was washed in the usual manner and dried at a temperature of from 30° to 40°.

I. 1·400 grm. burnt in an open porcelain basin gave 0·6487 peroxide of iron, corresponding to 32·1 per cent. iron.

II. 1·0365 grm. gave 0·481 peroxide of iron, corresponding to 32·0 per cent. iron.

III. 1·0035 grm. gave 0·463 peroxide of iron, corresponding to 31·8 per cent. iron.

Burned with chromate of lead,—

I. 0·6934 grm. gave 0·4405 carbonic acid and 0·1919 water, corresponding to 17·3 per cent. carbon and 27·9 per cent. water.

II. 0·415 grm. gave 0·269 carbonic acid and 0·127 water, corresponding to 17·7 per cent. carbon and 28·6 water.

III. 0·304 grm. gave 0·233 carbonic acid and 0·119 water, corresponding to 17·4 per cent. carbon and 20·0 water.

Nitrogen determination according to Will's method:—

I. 0·4065 grm. gave 0·3077 chloride of platinum and ammonium, corresponding to 20·2 per cent. nitrogen and 0·574 platinum.

II. 0·543 grm. gave 1·780 chloride of platinum and ammonium, corresponding to 20·6 per cent. nitrogen and 0·780 platinum.

The following table shows the degree of approximation to the formula $Fe_7\ Cy_9$:—

| | Calculated. | Found. | | |
|---|---|---|---|---|
| | | I. | II. | III. |
| $Fe_7$ | 190·4 = 31·56 | 32·1 | 32·0 | 31·8 |
| $C_{18}$ | 108·0 = 17·87 | 17·3 | 17·7 | 17·4 |
| $N_9$ | 126·0 = 20·83 | 20·2 | 20·6 | |
| $Aq_{20}$ | 180·0 = 29·74 | 27·9 | 28·6 | 28·0 |

In each combustion fresh-prepared substance was taken. The slight excess of iron and loss of carbon and nitrogen are doubtless to be attributed, in spite of the precautions taken to prevent it, to a decomposition having taken place during the drying, by which hydrocyanic acid was set free, as indeed might be recognised by the smell, and peroxide of iron formed. The oxygen combined with iron is in the table calculated as water, hence the deficiency of water. This decomposition, which takes place very easily, explains the formation of the so-called basic prussian blue, a substance considered as a compound of prussian blue and peroxide of iron, but of which little is known.

$$3\text{Cfy}\ 4\text{Fe} + 3\text{aq} - 3\text{CyH} = 2\text{Cfy}\ 3\text{Fe} + \text{Fe}_2\ \text{O}_3.$$

By the action of light a process of reduction takes place,

as was remarked above in the case of another compound. With other cyanogen compounds a similar action occurs, of which I will mention a striking instance further on. On decomposing this substance by potash, ferrocyanide of potassium is formed and peroxide of iron set free. Experiments, in which I endeavoured to determine quantitatively the proportion of iron separated by potash, invariably gave more than the formula of the pure substance requires, but this seems to be accounted for by the formation of the above-described basic compound.

In aqueous oxalic acid the prussian blue is very easily soluble. By the addition of carbonate of potash to this liquid the colour is changed to a red-brown, but no iron is precipitated at the ordinary temperature; as soon however as the liquid is boiled, peroxide of iron falls down in the proportion of three-fifths of that contained in the blue compound.

An unweighed quantity of dried prussian blue was dissolved in oxalic acid, and by boiling with carbonate of potash 0·208 peroxide of iron were precipitated. The liquid contained 0·137. The proportion of 3 to 2 requires 0·207 and 0·138. On a second determination 0·274 were precipitated by potash, whilst 0·174 remained in solution. The proportion of 3 to 2 requires 0·268 and 0·179. This reaction with oxalic acid might reward further examination. A remarkable circumstance connected with it is that the liquid after being filtered off from the peroxide of iron, separated by potash, is precipitated blue by muriatic acid.

I have now endeavoured to describe the formation of prussian blue under different circumstances, and the influence which these exercise on its composition, giving particular attention to the presence of potassium.

It appears to me that this circumstance of the presence of potassium is not a matter of mere scientific interest, but is also of great importance to the dyer, for it materially affects the colour and dyeing power of the product in the manner I shall now proceed to state. The greater the quantity of potassium contained in the cyanide, the lighter and more approaching to violet is its colour; and, on the other hand, in proportion as the quantity of potassium is diminished the colour becomes deeper and more powerful. Of the different blue compounds described above the brightest and most striking is that formed from the residue of the distillation of prussic acid, $\left(2\mathrm{Cfy}\left\{\begin{matrix}2\mathrm{Fe}\\ \mathrm{K}\end{matrix}\right.\right)$. Next to this in order stands the precipitate formed by proto-sulphate of iron in an excess of ferridcyanide of potassium, $4\mathrm{Cfy}\left\{\begin{matrix}5\mathrm{Fe}\\ \mathrm{K}\end{matrix}\right.$. The next link in the chain is a

compound formed by the decomposition of ferridcyanide of potassium by sulphuric acid, which contains still less potassium, and which I will presently describe. Darkest of all are the compounds which contain no potassium. The dyeing power of these substances, by which term I intend to designate the relative power of imparting a blue colour to any colourless substance with which they may be mixed, is in the inverse ratio to their quantity of potassium; but in such a manner that those containing potassium have a smaller colouring power than, after deducting the cyanide of potassium contained in them, would belong to the remainder; whence we see that the potassium plays no indifferent part in their colouring power.

When a solution of ferridcyanide of potassium is treated with concentrated sulphuric acid a green precipitate is formed, consisting of percyanide of iron and a small quantity of cyanide of potassium. By continued boiling with an excess of sulphuric acid its colour is changed into a rich blue. It is advisable to continue boiling for a considerable time after the change of the colour has taken place, in order to ensure the complete transformation. Ammonia, which may be easily proved to exist in the liquid, is here formed at the expense of a part of the cyanogen. This compound was washed and dried in the manner described in former instances, and gave on analysis to 1·962 peroxide of iron 0·049 sulphate of potash, which is one proportion of potassium to about sixty iron, too small a quantity of potassium to be considered as essential.

I. 1·464 grm. gave 0·702 peroxide of iron, corresponding to 33·25 per cent. iron.

II. 1·152 grm. gave 0·556 peroxide of iron, corresponding to 33·45 per cent. iron.

III. 0·549 grm. gave 0·266 peroxide of iron, corresponding to 33·61 per cent. iron.

Burned with chromate of lead,—

I. 0·481 grm. gave 0·306 carbonic acid and 0·131 water, corresponding to 17·3 per cent. carbon and 27·2 water.

II. 0·347 grm. gave 0·219 carbonic acid and 0·95 water, corresponding to 17·7 per cent. carbon and 27·0 water.

The following table shows the degree of approximation to the formula $Fe_5 Cy_6 + 13Aq$:—

| | Calculated. | Found. | | |
|---|---|---|---|---|
| | | I. | II. | III. |
| $Fe_5$ . . | 136 = 33·2 | 33·2 | 33·4 | 33·6 |
| $C_{12}$ . . | 72 = 17·6 | 17·3 | 17·7 | |
| $N_6$ . . | 84 = 20·5 | | | |
| 13Aq . | 117 = 28·6 | 27·2 | 27·0 | |

It is evident, from the quantity of water found, that less hydrogen was in the substance than calculated, and that a portion of peroxide of iron was contained in it.

It is decomposed by potash in the same manner as Turnbull's blue, which has been dried in the air; peroxide of iron is set free, and hydroferrocyanic acid combines with the potash, as described under that compound. The cause of this reaction, which seems irreconcileable with the composition 2Cfy 3Fe, lies in an oxidation of the iron taking place by the action of the air. We have seen above that Turnbull's blue retains a considerable quantity of water, and may assume that its elements are divided between the radical and the iron. Its formation is as follows:—

$$\left.\begin{matrix}2\text{Cfy}\,3\text{K}\\3\text{FeO}\\4\text{Aq}\end{matrix}\right\} = 2(\text{Cfy}\,\text{H}_2)\,\text{Fe}_3\,\text{O}_4 + 3\text{KO}.$$

The fresh precipitate behaves as such a compound; but after it has been dried in the air potash separates from it pure peroxide of iron instead of the magnetic oxide. This proves that, what indeed ensues with all protosalts of iron, oxidation takes place on exposure to the air. A consideration of the analytical results immediately shows that such an admixture of peroxide of iron is contained in it. The process of oxidation consists in 2 atoms of the cyanide taking up 1 atom of oxygen:

$$2\{2(\text{Cfy}\,\text{H}_2)\,\text{Fe}_3\,\text{O}_4\} + \text{O} = 4(\text{Cfy}\,\text{H}_2) + 3\text{Fe}_2\,\text{O}_3.$$

This formula expresses the elements contained in the substance after drying in the air. A more probable expression for its composition is however obtained, if the elements of three such compound atoms are arranged to 4 atoms of prussian blue and 1 atom peroxide of iron. An analogous compound to the pure unoxidated Turnbull's blue is that which I described under the name of ferridcyanide of iron and potassium, but which may as correctly be considered as a combination of 2 atoms hydroferrocyanic acid with 1 peroxide of iron and 1 potash. A strong support of this view is the fact that it contains 4 atoms of water, which are not expelled at 100°.

I have also examined a great number of precipitates formed by ferrocyanide of potassium with other metallic salts, and universally found, that whatever may be the method of precipitation, it is not possible to replace all the potassium by the metal made use of. Ferrocyanide of potassium was added to a great excess of sulphate of copper; the precipitate, which had the well-known red-brown colour, was found after complete washing to contain a considerable quantity of potassium. The corresponding dingy yellow precipitate of ferridcyanide

also contains potassium. On decomposing it by potash, ferridcyanide of potassium and oxide of copper are obtained, which proves that it is a true ferridcyanide, and not analogous to Turnbull's blue.

The reducing action of light shows itself most strikingly in the case of this precipitate. It had, after drying, been kept in large pieces in a glass bottle which stood for some time near a window. All the outsides of the pieces turned towards the light, became of a red-brown colour from the formation of ferrocyanide.

On treating the ferrocyanide of copper above described with sulphuretted hydrogen, no action at first seemed to take place; after some time however it commenced; and on the decomposition being completed a strongly acid solution was formed, which became gradually blue on exposure to the air. It gave a blue precipitate with perchloride of iron, but did not possess the characteristic reaction of hydroferrocyanic acid, for it was not precipitated by æther. On adding muriatic acid this reaction however immediately appeared. By standing over sulphuric acid it dried into a blue mass with a coppery lustre, which with water formed a liquid not unlike a solution.

On analysis it gave to 0·487 peroxide of iron 0·261 sulphate of potash. The formula, $4\mathrm{Cfy}\left\{\begin{matrix}7\mathrm{H}\\ \mathrm{K}\end{matrix}\right.$, requires 0·270 sulphate of potash to the quantity of iron found.

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March 30, 1846.—Anniversary Meeting.—The President in the Chair.

The following Report of the Council was read by the President, and subsequently ordered to be printed in the Society's Transactions:—

### *Annual Report of the Council.*

IN calling the attention of the Members to the state of the Society, the Council have the satisfaction of stating that since the last Anniversary 20 Members have been admitted, namely 18 ordinary Members and 2 Associates. The entire number on our list is 200; of whom 90 are resident and 95 non-resident, 6 Foreign Members and 9 Associates; making the income of the present year 275*l*. The disbursements have been less than usual, and leave an increasing balance in the hands of the Treasurer.

The arrangement by which the Society is accommodated with a room for meeting and a place for depositing its books and specimens by the Society of Arts, still continues to the

satisfaction, we believe, of both parties. It has been suggested that the Society of Arts would permit one of their officers to act in the capacity of Librarian to the Chemical Society. Such an accommodation would enable our members to receive books and journals at all times, and render our collection much more available.

During the last year the Society has lost by death four members,—Mr. Amos Swaysland of Crayford, Messrs. John T. Cooper, jun., Joseph Cooper, and Mr. Thomas Everitt.

Mr. Everitt received his chemical education in the laboratory of the late Professor Strömeyer of Göttingen, and afterwards entered upon the career of a public teacher of the science in London, which he pursued with much ability till disqualified by serious illness. The last public appointments he held were the Professorships of Chemistry in the Medical School of Middlesex Hospital and in the College of Civil Engineers at Putney. Mr. Everitt lent his aid at the foundation of the Chemical Society, and was an active member of its first Council. Although an unfrequent contributor to the scientific literature of his time, Mr. Everitt was well known to us all as an accomplished analyst, and to be much devoted to chemical inquiry. The Chemical Memoirs contain one communication by our lamented colleague*. Mr. Everitt did not outlive his forty-third year.

Since last report the Society has published Parts 13, 14 and 15 of their Memoirs and Proceedings, which completed the second volume, and also Part 16 of a new volume. The communications are twenty-nine in number, several of them containing investigations of great extent and value, and include the researches of Messrs. Playfair and Joule on Atomic Volume and Specific Gravity; Contributions to Actino-Chemistry, by Mr. Hunt; Researches on Styrole, and the products of its Decomposition, by Drs. Blyth and Hofmann; Contributions to the knowledge of Conjugate Compounds, by Dr. Kolbe; an Account of Toluidine, a New Organic Base, by Drs. Muspratt and Hofmann; and Electrical Inquiries, by Mr. J. Napier; besides shorter communications of interest by Mr. Richardson, Dr. Gregory, Col. Yorke, Mr. Warington, Mr. Graham, Drs. Tilley and Maclagan, Mr. Crum, Mr. De la Rue, Mr. Williamson, Professor Schönbein, Dr. Stenhouse, Messrs. E. F. and J. E. Teschemacher, and Professor Middleton of Agra.

The audited report of the Treasurer was also submitted to the Society.

* On the Leaf-stalks of Garden Rhubarb as a source of Malic Acid, vol. i. p. 193.

## AUDITORS' REPORT.

*Dr.* ROBERT PORRETT (*Treasurer*), *in Account with the Chemical Society of London.* *Cr.*

| | | £ | s. | d. |
|---|---|---|---|---|
| 1845. March 29. | To Balance from last Account | 337 | 14 | 4 |
| 1846. March 25. | To Subscriptions since received | 171 | 0 | 0 |
| | | £508 | 14 | 4 |

| | | £ | s. | d. |
|---|---|---|---|---|
| 1845. May 19. | By payment for Bookbinding | 1 | 17 | 7 |
| 19. | ——— for Brass Stamp, Ink, and Dabbers | 1 | 0 | 0 |
| 20. | ——— for a series of the 'Annales de Chimie,' bought at public auction | 5 | 5 | 0 |
| 18. | ——— for Rent to Society of Arts | 25 | 0 | 0 |
| 18. | ——— of Gratuity to Servants and Door-keeper | 1 | 10 | 0 |
| 1846. Feb. 28. | ——— for 24 Bottles with Ground Stoppers | 1 | 8 | 0 |
| March 12. | ——— for an Engraved Copper-plate, with Impressions therefrom | 3 | 7 | 0 |
| 25. | ——— for Scientific Journals, &c., English and Foreign | 16 | 8 | 0 |
| 25. | ——— for Stationery, Account-books, Postage Stamps, Envelopes, &c. | 1 | 10 | 9 |
| 25. | ——— of Poundage, &c. to Collector | 9 | 7 | 2 |
| 25. | By Balance to his Debit in new Account | 442 | 0 | 10 |
| | | £508 | 14 | 4 |

London, 25th March, 1846.

R. PORRETT, *Treasurer.*

We have examined the above Account and find it correct,

PHILIP J. CHABOT,
GEORGE D. LONGSTAFF, } *Auditors.*

The Society then proceeded to the election of Officers and Council for the ensuing year, when the following Gentlemen were declared duly elected:—

*President.*—Thomas Graham, Esq.

*Vice-Presidents.*—Arthur Aikin, Esq., William Thomas Brande, Esq., John Thomas Cooper, Esq., Richard Phillips, Esq.

*Treasurer.*—Robert Porrett, Esq.

*Secretaries.*—Robert Warington, Esq., George Fownes, Esq., Ph.D.

*Foreign Secretary.*—E. F. Teschemacher, Esq.

*Council.*—Walter Crum, Esq.; Warren De la Rue, Esq.; William Gregory, M.D.; Robert Hunt, Esq.; Sir Robert Kane, M.D.; H. B. Leeson, M.D.; William H. Pepys, Esq.; Lyon Playfair, Esq., Ph.D.; M. Scanlan, Esq.; John Stenhouse, Esq., Ph.D.; James Lowe Wheeler, Esq.; Lieut.-Col. Philip Yorke.

The thanks of the Society were severally voted to the President, Secretary, Officers and Council for their services during the past year.

Numerous interesting Chemical objects were exhibited by the Members.

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April 6, 1846.—The President in the Chair.

Isaac Deck, Esq. was elected a Member of the Society.

The following papers were read:—

## CLXVI. *On the Action of Hyponitric Acid upon Aqueous Solutions of Bromine and Chlorine.* *By* Dr. C. F. Schœnbein.

THE hydrobromic and hydrochloric acids being decomposed by nitric acid into water, hyponitric acid and bromine or chlorine, it appears little likely that by the combined action of bromine and hyponitric acid water will be decomposed, and the hydrobromic and nitric acids formed. Such however seems to be the case, as will be seen from the following statements.

1. If the fumes of hyponitric acid are made to pass into an aqueous solution of bromine, the brown yellow colour of that fluid will be soon discharged, and its odour of bromine as well as its bleaching power destroyed. The same solution on being mixed either with chlorine or peroxide of lead reassumes its former colour, bromine being eliminated under those circumstances. It is hardly necessary to add, that an aqueous solution of bromine is also discoloured by nitric acid holding some hyponitric acid dissolved. Having added to aqueous bromine a sufficient quantity of hyponitric acid, the liquid obtained contains no trace either of bromine or hyponitric acid, and is in every respect like a mixture of

dilute nitric and hydrobromic acids. From the facts stated, it appears that at the common temperature bromine and hyponitric acid on their being put in contact with water are transformed into hydrobromic and nitric acids, and according to the theory of the day, we must account for that reaction by admitting that water is decomposed under the circumstances mentioned.

2. A yellow aqueous solution of chlorine treated with hyponitric acid in the way indicated under § 1, loses its colour, odour and bleaching power, and has exactly the same properties enjoyed by a mixture of dilute hydrochloric and nitric acids. Hence it follows that hyponitric acid acts upon aqueous chlorine in the same way as it does upon an aqueous solution of bromine.

3. If into a bottle, having previously been charged with hydrochloric acid gas, some strong and pure nitric acid is introduced, the latter will, even at a temperature of 15° R. below zero, be rapidly decomposed, chlorine and hyponitric acid being eliminated and water formed. Adding to that mixture a sufficient quantity of water, both chlorine and hyponitric acid will entirely disappear, *i. e.* hydrochloric and nitric acid be reformed.

From the facts above stated, it follows,—

*a.* That concentrated nitric and hydrochloric acids decompose each other into hyponitric acid, chlorine and water, even at very low temperatures.

*b.* That a sufficient quantity of water being present, chlorine or bromine, conjointly with hyponitric acid, decompose water (according to the theory of the day), forming nitric and hydrochloric or hydrobromic acid.

*c.* That nitric and hydrochloric or hydrobromic acid being dissolved in a sufficient quantity of water, can at the common temperature coexist without decomposing each other.

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## CLXVII. *On the Substances contained in the* Roccella tinctoria. *By* Edward Schunck, *Esq.*

THE *Roccella tinctoria* derives its interest from the fact of its being that species of lichen from which the finest kind of archil is prepared. It has been examined by Heeren and Kane. The former discovered in it a peculiar substance, which he called *Erythrin*, and a fat acid named by him *Roccellic acid*. The latter extracted from the plant a substance which he called *Erythrilin*, similar in properties to Heeren's erythrin, and a body to which he applied the name of *Ery-*

*thrin*, but which possesses all the properties of the substance called by Heeren *Pseuderythrin*, and supposed by him to be a product of the action of boiling alcohol on his erythrin. My results do not agree entirely with those of either of these chemists.

The lichen which I employed for my investigation was obtained from Angola and Madagascar, and was pronounced by a distinguished botanist, to whom I submitted it, to be the *Roccella tinctoria* var. *fuciformis*. In order to extract the various substances contained in it, I submitted it to the following operations:—

The plant was cut into pieces and treated in a capacious vessel with boiling water. After the boiling had continued for some time, the fluid, which had acquired a yellowish-brown colour, was strained through cloth. On cooling there was deposited from it a white substance in flocks and minute crystals. It was separated by filtration and washed with cold water. After drying it had a grayish appearance. In order to purify it, it was only necessary to dissolve it in boiling alcohol, which left behind an inconsiderable black or brown residue. On cooling it separated as a white crystalline mass. This substance resembles Heeren's erythrin and Kane's erythrilin. I shall call it *Erythric acid*.

The fluid from which this substance had separated was of a light brown colour. On evaporation it became dark brown and muddy, and left at length a dark brown viscid mass, having a sweetish bitter taste. This mass, after standing for some time, became solid and crystalline. It was treated with cold water, which left behind a crystalline substance of a brownish-white colour and a bitter taste. This substance is a product of the action of boiling water on erythric acid. I shall call it *Picro-erythrin*. In order to purify it, it must be, after washing it with a little cold water, dissolved in boiling water, to which is added some animal charcoal. After filtration and evaporation there remains a yellowish mass, which soon becomes crystalline and white. On treating this mass with cold water, the picro-erythrin remains behind perfectly white and in a state of purity.

To the brown fluid obtained by treating the dark brown mass with cold water, a solution of sugar of lead was added, which produced a copious grayish-brown precipitate. This precipitate, after being separated by filtration and washed with water, was decomposed by a stream of sulphuretted hydrogen gas. A light yellow fluid was obtained, which, on evaporation, became gradually brown and deposited a dark brown substance, insoluble in water but soluble in alcohol

and alkalies. A brown viscid mass was left at last, having an acid reaction and a strongly acid and at the same time bitter taste. It showed no trace of anything crystalline even after long standing. It was soluble in alcohol, but insoluble in æther. Its aqueous solution was precipitated by a solution of glue, by lime and baryta water, and acetate of copper, and was rendered muddy and gradually precipitated by sulphuric acid and common salt. It therefore consisted probably of some kind of tannic acid. Through the fluid separated from the precipitate produced by sugar of lead sulphuretted hydrogen gas was passed until all the lead was precipitated. The filtered fluid gave a slight flocculent precipitate on the addition of alcohol, but none with lime and baryta water or sulphuric acid. On evaporation it left a clear brown syrup, which soon changed into a crystalline mass, having a sweetish bitter taste. It contained besides picro-erythrin, to which it owed its bitter taste, a quantity of orcin, which was detected in the following manner:—A part of it was dissolved in boiling water, and during the boiling a quantity of magnesia was introduced into it. After filtration the fluid was evaporated to dryness. It left a brown mass, which no longer became crystalline on standing. The picro-erythrin had entered into combination with the magnesia, and on treating the mass with æther in the cold, a yellowish-brown fluid was obtained, which on evaporation gave crystals of orcin, recognisable by its well-known properties. The dark brown viscid mass obtained from the mother-liquor of the erythric acid left on being burnt a considerable quantity of ashes, consisting of sulphate of soda, chloride of sodium, oxide of iron and carbonate of magnesia, with a trace of carbonate of lime.

The lichen, after being extracted with boiling water, had lost its grayish-white colour and become green. It was dried and then treated with boiling alcohol. The alcohol acquired during the process a dark emerald-green colour. It was strained through cloth while still hot. On becoming cold it deposited a green flocculent substance, which was separated by filtration. The green colour of this substance could not be removed by washing with cold alcohol. On drying it became dark green and coherent, but when powdered it was light green again. This substance is a kind of fat; it cannot be fused without being decomposed. When heated on platinum foil it melts to a brown fluid, giving off at the same time a strong smell of burning fat, and burns without leaving any ashes. Heated in a tube closed at one end it melts and gives a brown, oily sublimate, which soon solidifies, but without becoming crystalline. It is left behind on evaporating its al-

coholic solution as an amorphous green mass. It is precipitated from its solution in alcohol by water, and also by an alcoholic solution of acetate of lead. It is insoluble in boiling muriatic and dilute sulphuric acids. Concentrated sulphuric acid dissolves it. Boiling nitric acid, even if dilute, destroys its green colour and makes it yellow. If treated with concentrated nitric acid, it is dissolved and decomposed with an evolution of nitrous acid; by degrees there collect on the surface of the fluid yellow oily drops, which solidify on cooling. It is very little soluble in boiling caustic ley, and insoluble in ammonia. The dark green fluid from which this substance had separated was evaporated to dryness, when it left a dark green viscid residue, interspersed with yellowish crystalline grains. This residue was treated with boiling water, which removed some picro-erythrin contained in it, and then with cold alcohol, which left behind a quantity of the greenish-white fat just described, and acquired a dark green colour. The alcoholic fluid had an acid reaction. It contained roccellic acid and a dark green, easily fusible fat. In order to separate the roccellic acid, an alcoholic solution of sugar of lead was added. This produced a greenish-white flocculent precipitate, which was separated by filtration and washed with alcohol. This precipitate, consisting of roccellate of lead, was decomposed by dilute nitric acid, which left the roccellic acid behind of a green colour. The latter, after being washed with water to remove the nitrate of lead, was dissolved in boiling alcohol, to which some animal charcoal was added. After filtering the solution, the roccellic acid separated on cooling in white crystalline needles. By adding water to the green alcoholic fluid from which the roccellate of lead had been precipitated, it became milky, and on boiling, dark green drops of a fatty substance collected at the bottom. This substance is a kind of fat, which is easily fusible at the temperature of boiling water. Its green colour is no doubt owing to the presence of chlorophyll, which cannot however be separated from it. It imparts no colour to boiling muriatic or dilute sulphuric acid. Boiling nitric acid destroys its green colour and changes it into yellow, after which it dissolves in alcohol with a yellow colour. It is soluble in alkalies, and is precipitated again by acids.

The lichen, after extraction with water and alcohol, was treated with dilute caustic ley at a boiling heat. A dark brown fluid was obtained, to which, after filtration, muriatic acid was added. This produced a dark brown flocculent precipitate, which, after filtering, washing with water and drying, appeared as a light brown powder. When heated it

burns without leaving any ash. On being treated with strong caustic potash at a boiling heat, it gives off a slight smell of ammonia. It is soluble in alkalies, but insoluble in alcohol. The acid fluid from which it was precipitated deposited on evaporation a dark brown substance, in the same way as a solution of tannin or extractive matter. It is doubtful indeed whether the brown substance precipitated by the acid from the alkaline fluid is contained in the plant as such, or whether it is formed by the conjoint action of the air and alkali on some other substance in the lichen.

The *Roccella tinctoria* is easily reduced to ashes. These ashes are grayish-white. They consist of sulphate of soda, chloride of sodium, oxide of iron, alumina, carbonate of lime and carbonate of magnesia.

I shall now proceed to describe more fully several of the substances just mentioned.

### *Erythric Acid.*

This body is the most important of those existing in the plant, as it is that one which gives rise to the colouring matters for the production of which the lichen is employed. It is not possible however to obtain much from the plant, since by the action both of boiling water and alcohol it undergoes a rapid change. By the method described above I obtained in one case from 1 lb. of the lichen 60 grains of it. If prepared without the intervention of alkalies, erythric acid is perfectly white and tasteless. It is soluble in water, alcohol and æther. 1 part dissolves in 240 parts of boiling water, from which a great part separates on cooling in flocks, or as a crystalline powder. Its solubility in æther distinguishes it from Heeren's erythrin, and its solubility in water from Kane's erythrilin. Its solutions redden litmus paper. From a concentrated solution in boiling alcohol it is deposited on cooling in needles and star-shaped masses, which consist of minute crystals. It is precipitated from its alcoholic solution by water as a jelly. If the alcoholic solution however be boiled for a length of time, it is converted into erythric æther, in the same way as lecanoric acid is converted by boiling alcohol into lecanoric æther; and if water be now added to the solution no precipitate is formed, but the erythric æther gradually crystallizes in needles from the solution. By the continued action of boiling water erythric acid is converted into picroerythrin. Heated on platinum foil, it melts and burns away without leaving any residue: heated in a tube closed at one end, it gives an oily sublimate, which after some time crystallizes; this sublimate consists of orcin. Erythric acid is

easily soluble in caustic and carbonated alkalies, and in lime and baryta water, and it is reprecipitated from these solutions by acids in form of a jelly, unless they have previously been boiled or left to stand for a considerable time. If a solution of it in baryta water be boiled, carbonate of baryta is deposited, and acids now produce no precipitate of erythric acid. If the excess of baryta be removed by a stream of carbonic acid gas, and the filtered solution be evaporated, there are obtained prismatic crystals, which are easily recognised as consisting of orcin by their intensely sweet taste, by their being volatilizable without any residue, by their solution precipitating basic acetate of lead, reducing chloride of gold, and giving a red colour with ammonia and red flocks on boiling with nitric acid. Erythric acid then, like lecanoric, is converted by alkalies into orcin and carbonic acid. A solution of erythric acid in ammonia exposed to the air soon becomes of a dark-red or purple colour. It is the basis, and I believe the only one, of the colouring matters derived from the plant. An alcoholic solution of erythric acid is not precipitated by nitrate of silver, but the addition of nitrate of silver to an ammoniacal solution produces a white precipitate, which on boiling becomes black, a mirror of silver being formed at the same time on the sides of the glass. Chloride of gold added to an alcoholic solution is not changed even on boiling. With perchloride of iron an alcoholic solution strikes a deep purple colour; on the addition of ammonia the colour is changed into yellow, but the oxide of iron is not precipitated, unless the fluid be boiled. It is not precipitated by an alcoholic solution of acetate of lead, but basic acetate of lead produces immediately a copious precipitate.

On combustion with oxide of copper the following results were obtained:—

I. 0·5400 grm. dried at 212° gave 1·1640 carbonic acid and 0·2530 water.

II. 0·3640 grm. gave 0·7835 carbonic acid and 0·1820 water.

These numbers lead to the following composition:—

| | | Calculated. | I. | II. |
|---|---|---|---|---|
| 34 equivs. Carbon . | 2550·0 | 59·47 | 58·78 | 58·70 |
| 19 ... Hydrogen | 237·5 | 5·53 | 5·20 | 5·55 |
| 15 ... Oxygen . | 1500·0 | 35·00 | 36·02 | 35·75 |
| | 4287·5 | 100·00 | 100·00 | 100·00 |

The lead compound was prepared by precipitating an alcoholic solution of erythric acid with basic acetate of lead, filtering, washing the precipitate with cold water and drying *in vacuo*.

I. 0·6340 grm. gave 0·6435 carbonic acid and 0·1215 water. 0·3465 gave 0·0075 lead and 0·1970 oxide of lead.

II. 0·3195 grm. gave 0·3160 carbonic acid and 0·0630 water. 0·4345 gave 0·0945 lead and 0·2520 oxide of lead.

This gives—

| | | Calculated. | I. | II. |
|---|---|---|---|---|
| 34 eqs. | Carbon . . 2550·0 | 27·08 | 27·68 | 26·97 |
| 15 ... | Hydrogen . 187·5 | 1·99 | 2·12 | 2·19 |
| 11 ... | Oxygen . . 1100·0 | 11·69 | 11·04 | 11·72 |
| 4 ... | Oxide of lead 5578·0 | 59·24 | 59·16 | 59·12 |
| | 9415·5 | 100·00 | 100·00 | 100·00 |

The decomposition of erythric acid by means of alkalies is therefore as follows:—

1 equivalent of erythric acid . $= C_{34} H_{19} O_{15}$
$-2$ equivalents of carbonic acid . $= C_2 O_4$
$+3$ equivalents of water . . . $= H_3 O_3$, gives
2 equivalents of crystallized orcin $= C_{32} H_{22} O_{14}$.

### *Erythric Æther.*

This body has all the properties ascribed to pseuderythrin by Heeren and Kane, and as I found its composition to differ very little from that given by Liebig for Heeren's pseuderythrin, and by Kane for his erythrin, it can hardly be supposed that it is a different body. It is easily prepared by the action of boiling alcohol on erythric acid, in the same way as lecanoric æther from lecanoric acid. Indeed its formation takes place so easily and rapidly in this way, that it is almost impossible to extract erythric acid from the plant by means of boiling alcohol, nothing being obtained by endeavouring to obtain it in this way but erythric æther. In its appearance and properties erythric æther can hardly be distinguished from lecanoric æther, and as its composition in 100 parts happens to be almost the same, the one may easily be mistaken for the other. Erythric æther is at first tasteless, but after being kept for some time in the mouth, it produces a burning sensation on the tongue. It is soluble in boiling water. If more of the substance be taken than the water can dissolve, the excess melts, forming drops like oil, which sink to the bottom. On cooling the solution becomes milky, and a great part of the æther crystallizes out in needles and plates. It is easily soluble in alcohol and æther. On allowing the alcoholic solution to evaporate spontaneously, it is obtained in prismatic crystals. When heated in a tube it melts, and is almost completely volatilized, the vapour condensing in the colder parts of the tube to a fluid which soon

crystallizes. It is soluble in caustic and carbonated alkalies, and in lime and baryta water. From these solutions it is precipitated unchanged by acids, unless they have previously been boiled for a length of time. It reduces nitrate of silver on the addition of ammonia and boiling, and chloride of gold without the addition of any alkali. It gives a precipitate with basic acetate, but none with neutral acetate of lead. On dissolving a quantity of it in caustic potash and subjecting the fluid to distillation, I obtained in the receiver a fluid, from which, on the addition of dry carbonate of potash, a thin layer of alcohol separated, which was easily recognised by its peculiar spirituous smell and its burning with a blue flame. The fluid in the retort was neutralized with sulphuric acid and evaporated to dryness. The residue was treated with alcohol, which on evaporation gave crystals of orcin. Its products of decomposition with alkalies are therefore the same as those of lecanoric æther. Its analysis gave the following results:—

I. 0·5380 grm. gave 1·1965 carbonic acid and 0·2970 water.

II. 0·4085 grm. gave 0·9095 carbonic acid and 0·2260 water.

These numbers correspond to the following composition:—

| | | | Calculated. | I. | II. |
|---|---|---|---|---|---|
| 38 equivs. | Carbon . | 2850·0 | 61·45 | 60·65 | 60·72 |
| 23 ... | Hydrogen | 287·5 | 6·19 | 6·13 | 6·14 |
| 15 ... | Oxygen . | 1500·0 | 32·36 | 33·22 | 33·14 |
| | | 4637·5 | 100·00 | 100·00 | 100·00 |

Its rational formula is $C_{14}\,H_{18}\,O_{14} + C_4\,H_5\,O$. It is therefore formed from erythric acid by the substitution of 1 equivalent of oxide of ethyl for 1 equivalent of water.

### *Picro-erythrin.*

This substance is a product derived from erythric acid. To it must be attributed the highly bitter taste of all the extracts made of the lichen, whether aqueous or alcoholic. In its properties, however, it agrees strictly neither with the erythrin-bitter of Heeren nor the amarythrin of Kane. It approaches nearest to the telerythrin of the latter, according to the description given by him of that substance. It is a product of the action of water on erythric acid. If pure erythric acid, as prepared by the process described above, be treated with boiling water for a short time, it dissolves, the fluid acquires a bitter taste, and on cooling deposits no erythric acid. On evaporation it leaves a brownish, viscid mass, leaving a taste between bitter and sweet. This mass, after

some time, becomes crystalline. It may then be treated with cold water, which leaves the picro-erythrin behind white and pure. I have described above how it may be obtained as a secondary product in the preparation of erythric acid. In operating on the plant with boiling water much more is obtained of it than of erythric acid. On extracting the lichen also with boiling alcohol, a considerable quantity is found in the extract. Picro-erythrin has the following properties. It has a strong but not disagreeably bitter taste. It is soluble in water, alcohol and æther. Its solubility in æther distinguishes it from Kane's amarythrin and telerythrin, which are insoluble in that fluid. It does not dissolve readily in cold water, but easily in boiling water. Its solution in the latter, however, does not re-deposit it on cooling. On evaporating a solution of it in water or alcohol, it is left behind as a white crystalline mass, but never in well-defined crystals or needles. Its solutions redden litmus paper slightly. It does not undergo any further change on being treated with boiling water, nor does it form an æther on being treated with boiling alcohol, as erythric acid does; it has therefore little or no claim to be considered as an acid. Heated on platinum foil it melts to a yellow fluid, is decomposed, and burns with a bright flame, leaving no ash. Heated in a tube closed at one end it gives a sublimate of orcin. It is decomposed by boiling nitric acid with an evolution of nitrous acid. Concentrated sulphuric acid dissolves it, and on boiling decomposes it with a disengagement of sulphurous acid. It dissolves in caustic alkalies, and in lime and baryta water in the cold. Its solution in baryta water deposits carbonate of baryta on boiling, and the solution then contains nothing but orcin. Its solutions in alkalies speedily become red on exposure to the air. Its aqueous solution is not precipitated by neutral acetate, but copiously by basic acetate of lead. With perchloride of iron it gives a deep purple colour, which is destroyed by ammonia, the oxide of iron being immediately precipitated. Nitrate of silver is not changed by it on boiling, but on the addition of ammonia a precipitate is produced, which on boiling the fluid is reduced, the silver being deposited as a metallic mirror on the sides of the glass. Chloride of gold is slowly reduced by it on boiling, the gold being deposited in the shape of metallic scales; if caustic potash be added the reduction is effected instantaneously, the gold being deposited as a black powder. It gives no precipitate with a solution of glue. Its analysis gave the following:—

I. 0·5090 grm. gave 0·9830 carbonic acid and 0·2850 water.
II. 0·4690 grm. gave 0·8970 carbonic acid and 0·2510 water.

These numbers give the following composition:—

| | | | Calculated. | I. | II. |
|---|---|---|---|---|---|
| 34 equivs. | Carbon . . | 2550 | 52·57 | 52·86 | 52·16 |
| 24 ... | Hydrogen . | 300 | 6·18 | 6·22 | 5·94 |
| 20 ... | Oxygen . . | 2000 | 41·25 | 40·92 | 41·90 |
| | | 4850 | 100·00 | 100·00 | 100·00 |

The compound with oxide of lead, prepared by precipitation with basic acetate of lead, gave the following results:—

0·2575 grm. gave 0·1465 carbonic acid and 0·0130 water.

0·3185 grm. gave 0·0220 lead and 0·1960 oxide of lead.

This corresponds to—

| | | | Calculated. | Found. |
|---|---|---|---|---|
| 34 equivs. | Carbon . . | 2550 | 15·93 | 15·51 |
| 24 ... | Hydrogen . | 300 | 1·87 | 1·85 |
| 20 ... | Oxygen . . | 2000 | 12·51 | 13·70 |
| 8 ... | Oxide of lead | 11156 | 69·69 | 68·94 |
| | | 16006 | 100·00 | 100·00 |

Erythric acid, therefore, in its conversion into picro-erythrin, takes up the elements of 5 equiv. of water.

### *Roccellic Acid.*

This acid was discovered by Heeren. If the lichen be extracted with ammonia in the cold, a yellow fluid is obtained which contains erythric acid and roccellic acid dissolved in ammonia. The roccellic acid may be separated by adding chloride of calcium to the fluid, by which a precipitate of roccellate of lime is produced, or by precipitating the two acids with muriatic acid and treating the precipitate with boiling water, which dissolves the erythric acid and leaves the roccellic acid behind. But by this method the acid is not obtained so pure as by extraction with alcohol, as the ammonia takes up at the same time a brown substance from the plant, from which it is afterwards difficult to separate the acid. I therefore prefer the method which I have described above.

Roccellic acid is a species of fat acid. I have nothing to correct in, and little to add to, the description given of it by Heeren. It is insoluble in water, but easily soluble in alcohol and æther. From a hot concentrated solution in alcohol it crystallizes on cooling in small needles, forming when dry a white, shining crystalline mass. By the spontaneous evaporation of its alcoholic solution, it is obtained in larger and more defined crystals. Its solutions redden litmus paper strongly. Heated on platinum foil it melts to a transparent fluid, which, if allowed to cool, congeals again to a crystalline mass. If further heated it is decomposed, giving off a smell like burning fat, and burns with a bright flame, leaving no residue. Heated in a tube closed at one end, it melts and

gives an oily sublimate, leaving little or no residue; the oily sublimate is soon changed into a crystalline mass, but on being again sublimed it remains fluid. Roccellic acid is insoluble in dilute mineral acids, but soluble in alkalies. When caustic potash is poured on it, it swells up to a gelatinous mass, which is insoluble in the caustic ley, but soluble in water. The solution on boiling foams like a solution of soap; strong acids re-precipitate the roccellic acid in flocks. The solution on evaporation leaves a crystalline, saponaceous mass. Ammonia behaves in a similar manner. It is also soluble in carbonated alkalies, carbonic acid being disengaged on boiling, but it is insoluble in lime and baryta water. The solution in ammonia gives with chloride of calcium and chloride of barium flocculent precipitates, consisting of roccellate of lime and baryta. A solution of roccellic acid in alcohol is precipitated by an alcoholic solution of acetate of lead, but not by a solution of nitrate of silver. A solution of it in ammonia gives with nitrate of silver a white gelatinous precipitate, which becomes brown when the fluid is boiled, but is not completely reduced. An alcoholic solution of roccellic acid does not reduce chloride of gold on boiling.

On being ignited with oxide of copper—

I. 0·42100 grm. gave 1·0200 carbonic acid and 0·4025 water.
II. 0·2815 grm. gave 0·6795 carbonic acid and 0·2720 water.

From these numbers the following composition may be deduced:—

| | | | Calculated. | I. | II. |
|---|---|---|---|---|---|
| 24 equivs. | Carbon . . | 1800·0 | 66·97 | 66·07 | 65·83 |
| 23 ... | Hydrogen | 287·5 | 10·69 | 10·62 | 10·73 |
| 6 ... | Oxygen . | 600·0 | 22·34 | 23·31 | 23·44 |
| | | 2687·5 | 100·00 | 100·00 | 100·00 |

The lead salt was prepared by dissolving the acid in a small quantity of ammonia and precipitating with acetate of lead.

I. 0·4475 grm. gave 0·5530 carbonic acid and 0·2070 water.
0·3405 grm. gave 0·0705 lead and 0·0990 oxide of lead.
II. 0·4360 grm. gave 0·5490 carbonic acid and 0·2025 water.
0·2860 grm. gave 0·0730 lead and 0·0675 oxide of lead.

These numbers correspond to the following composition:—

| | | | Calculated. | I. | II. |
|---|---|---|---|---|---|
| 24 equivs. | Carbon . . | 1800 | 33·55 | 33·70 | 34·34 |
| 22 ... | Hydrogen . | 275 | 5·12 | 5·13 | 5·16 |
| 5 ... | Oxygen . . | 500 | 9·34 | 9·81 | 9·42 |
| 2 ... | Oxide of lead | 2789 | 51·99 | 51·36 | 51·08 |
| | | 5364 | 100·00 | 100·00 | 100·00 |

This salt is therefore basic. I have been prevented by want of material from examining the other salts of the acid.

April 20, 1846.—The President in the Chair.

The following presents were announced:—

"On the Gases evolved from Iron Furnaces, with reference to the Theory of Smelting Iron," by Drs. Bunsen and Playfair, from the authors.

"On the Nature and Causes of the Disease in Potatoes," by Lyon Playfair, Esq., Ph.D., from the author.

"Report on the State of large Towns in Lancashire," by Lyon Playfair, Esq., Ph.D., from the author.

Dr. C. F. Schœnbein was elected a Foreign Member; John Thomas Way, Esq., and James Thomas Jullion, Esq., Members of the Society.

The following papers were then read:—

## CLXVIII. *On the Constitution of Aqueous Solutions of Acids and Alkalies.* By John Joseph Griffin, Esq.

AN inquiry has been instituted of late into the *volume* that is assumed by a given weight of any chemical substance on being dissolved in water; and the chemists who have instituted this inquiry have promptly drawn conclusions and established laws, very general and comprehensive in character, and susceptible of important applications, provided they are founded on well-established facts.

Thus, "in the year 1840," I quote from Messrs. Playfair and Joule, "Dalton made the interesting discovery, that sugar and certain salts on being dissolved in water increase its bulk only by the amount of water pre-existing in them. He generalized this observation by asserting that all hydrated salts dissolve in water, increasing its bulk merely by their amount of water of hydration, while anhydrous salts do not at all increase the bulk of the water in which they are dissolved.

"But it must not be forgotten, that when Dalton published this paper he was much enfeebled by illness, and on this account it does not derogate from the acuteness of the philosopher, that Mr. Holker was unable to confirm Dalton's results in repeating the experiments in 1843. He did so however in the case of sulphate of magnesia, and approximately in that of one or two other salts."—*Memoirs of the Chemical Society*, vol. ii. p. 404.

The experiments that were particularly described by Dalton, were made with sugar and sulphate of magnesia. But he declares that his hypothesis was not founded on those experiments alone. He says, "I have tried the carbonates, the sulphates, the nitrates, the muriates or chlorides, the phos-

phates, the arseniates, the oxalates, the citrates, the tartrates, the acetates, &c. &c., and have been uniformly successful. Only the water adds to the *bulk* and the *solid matter* adds to the weight."—*Essay on the quantity of Acids, Bases and Water in the different varieties of Salts; with a new method of measuring the* WATER *of Crystallization, as well as the* ACIDS *and* BASES.

Dr. Dalton knew well the importance of the principle he was attempting to establish, for he declares "It is the greatest *discovery* that I know of next to the atomic theory." —*New and Easy Method of Analysing Sugar.*

In May 1845, Messrs. Playfair and Joule presented to the Chemical Society a memoir, in which they have recorded the results of an elaborate experimental examination of Dalton's hypothesis. (Memoirs of the Chemical Society, vol. ii. p. 401–481.) Their conclusions are no less startling than were those of Dalton, on which the inquiry proceeded. They find his doctrine in relation to sugar to be true. "It is," they say, "an extraordinary fact, that the twelve atoms of carbon in sugar cease to occupy space in solution, and that the bulk of an atom of sugar is just the bulk of its oxygen and hydrogen considered as water. And this," they say, "is a matter of supreme interest, and cannot fail to lead to important results when we come to the consideration of organic compounds." —*Pages* 478 *and* 422.

They next confirm Dalton's statement with regard to sulphate of magnesia and other analogous salts, namely, that when anhydrous they occupy no space in solution, but when hydrated they add the bulk of the water of hydration to the bulk of the water of solution.

Thirdly, they find that other compounds dissolved in water increase its volume for every equivalent, either by 9 or by multiples of 9. [9 is their standard number for the volume of an equivalent of water.]

These statements affirm three main propositions, namely,—

1. That certain anhydrous substances when dissolved in water *occupy no space*. The volume of the solution is the same as the volume of the water contained in it.

2. That other anhydrous substances when dissolved in water *assume a fixed and characteristic volume*; so that the volume of the solution is not the same as that of the water contained in it, but greater or smaller, in exact proportion to the atomic volume of the substance dissolved in it.

3. That when organic substances are dissolved in water their carbon occupies no space, but their hydrogen and oxy-

gen, if in the proportions proper to form water, occupy exactly the space of an equivalent weight of water.

Other subjects than these are discussed in the memoir of Messrs. Playfair and Joule, but in order to avoid complication I shall confine myself entirely to what relates to the atomic volume of substances in solution.

If the first two of the foregoing propositions are true, they give us important information respecting the constitution of aqueous solutions. If, for example, we are furnished with the specific gravities of anhydrous substances, and with their atomic volumes in solution, then, knowing their atomic weights, and taking for granted the specific gravity of water and the temperature of the several materials, we shall have in our hands the whole laws that regulate the specific gravities of aqueous solutions, and we shall be enabled to calculate tables of solutions perfectly free from the inaccuracies that beset all tables that are prepared from experiments on individual solutions. We shall be rendered by these doctrines so completely master of details, that, if the specific gravity of any solution be given, we shall be able to tell its chemical strength; or if the chemical strength be given, we shall be able to declare what must be its specific gravity. These doctrines lead, therefore, to very important practical results, and they are the more deserving of regard, that the previous researches of chemists in this department have been entirely unsuccessful. All that we know of the relation of the chemical strength of solutions to their specific gravity has been derived from practical trials, and we have no general principle to guide us beyond the limits of those trials, no rule by which to test the accuracy of the experimental data, or by which to determine either the chemical power of a solution from its density, or the density from its chemical power. The laws announced by Dalton, and reaffirmed by Messrs. Playfair and Joule, come apparently to clear away this difficulty, and coming supported by the results of a series of elaborate and ingenious experiments, if they are too startling to command the immediate assent of chemists, they at least merit a rigorous examination.

In the course of an inquiry into the subject of centigrade testing (dosage), I have had occasion to examine the constitution of a great number of solutions of the principal acids and alkalies. The facts elicited by that examination afforded collectively a sharp test of the accuracy of these new doctrines respecting the atomic volumes of substances in solution. I compared therefore the doctrines with the facts care-

fully, and I feel bound to declare that they are at variance. Among a dozen chemical substances, whose solutions I have examined, I find only one that appears to have a fixed atomic volume in solution in water. That substance is ammonia. All the other substances that I have examined vary constantly in their liquid volume, according to the state of dilution, and I am forced to the conclusion, in so far at least as concerns the substances that I shall enumerate, that the doctrine of a fixed atomic volume in solution is fallacious and of no use. While I think it right to state this opinion explicitly, I do so with considerable diffidence. It is possible that I may have overlooked some circumstance essential to the full comprehension of the question. I by no means deny the accuracy of the experiments upon which the opposite opinion has been founded. The difference in our conclusions results from different ways of interpreting the experiments. The conclusions are however incompatible; and if the doctrines of Messrs. Playfair and Joule shall prove to be correct, serious fallacies must exist in my calculations or mode of reasoning.

To place the evidence on this subject before chemists, I proceed to detail my researches into the constitution of solutions of acids and alkalies. An investigation of this sort has the unfortunate property, that, dealing with a great variety of separate facts, an account of it must necessarily be long. I shall shorten it to the utmost by throwing as much as possible into the form of Tables; and in order to render the condensed account intelligible, I shall begin by describing the plan of the Tables, and explaining such terms and other particulars as seem to require it.

### *Of the Measures used.*

I have in all cases examined the constitution of the same volume of solution, namely, the tenth part of an imperial gallon, or the bulk of one avoirdupois pound, or 7000 grains of pure water at the temperature of 62° F. I propose to call this measure a DECIGALLON.

For the sake of having a manageable term for a small volume of liquid, I divide the decigallon into 1000 parts, each of which contains 7 grains of water, and for which measure I propose the name of SEPTEM.

A complete scheme of decimal measures thus founded on the imperial gallon is exhibited in the following Table:—

*Imperial Liquid Measure. Divided Decimally.*

| Gallon. | Deci-gallons. | Centi-gallons. | Milli-gallons. | Septems. | Avoirdupois weight of water at 62° F. | |
|---|---|---|---|---|---|---|
| | | | | | Grains. | Pounds. |
| 1· | 10· | 100· | 1000· | 10000· | 70000· | 10· |
| ·1 | 1· | 10· | 100· | 1000· | 7000· | 1· |
| ·01 | ·1 | 1· | 10· | 100· | 700· | ·1 |
| ·001 | ·01 | ·1 | 1· | 10· | 70· | ·01 |
| ·0001 | ·001 | ·01 | ·1 | 1· | 7· | ·001 |

1 Quart = 2500 Septems. 1 Fluid ounce = 62·5 Septems.
1 Pint = 1250 Septems. 1 Cubic inch = 36·06543 Septems.

The relation of the decigallon to the septem is the same as that of the litre (kilogramme of water) to the cubic centimetre (gramme of water).

1 litre contains 2200 septems.

*Chemical Standards.*

In speaking of chemical substances with reference to atomic weights, I have used the numbers contained in the tables of Berzelius, oxygen = 100. In order to be able to speak without vagueness of certain absolute quantities of substances, I use the term *Test Atom* to signify Berzelius's atomic weight of a substance *weighed in English grains.* By the term *Degree,* I mean the hundredth part of a test atom. Thus,—

5·01165 grs. is 1° of $SO^3$.
501·165 ... is 1 test atom, or 100° of $SO^3$.

In applying these measures and weights to centigrade testing, I prepare *normal test liquors* of 100° of strength, in all cases, by dissolving 1 test atom of the substance in so much water as produces 1 decigallon of solution at 62° F.; that is to say,—

*To prepare Carbonate of Soda of* 100°.—I dissolve 667·335 grs. of pure anhydrous carbonate of soda in distilled water, dilute the solution to the bulk of about 995 septems, bring it to the temperature of 62° F., and then adjust the volume to exactly 1000 septems.

*To prepare Nitrate of Silver of* 10°.—I dissolve 212·864 grs. of pure crystallized nitrate of silver in distilled water, and in like manner dilute the solution at 62° F. to the bulk of 1000 septems.

A centigallon of test liquor of 100° contains the tenth part of a test atom of any substance. My alkalimeter, or centigrade pouret, has the capacity of a centigallon, and is graduated into 100 septems: hence every degree of this instrument indicates the 1000th part of the test atom of the reagent, while,

as each degree measures the 10,000th part of an imperial gallon, it is easy to find the relation between the chemical strength and the physical mass of a given solution.

### *Methods of Experimenting.*

The experiments that are distinguished in the following Tables by the letter G were made in my laboratory, except in those cases where other authorities are specified. The chemical solutions were prepared in stoppered graduated glasses at the temperature of 62° F. The requisite analyses were all effected by the method of centigrade testing. Various precautions were taken to ensure accuracy, but I forbear to enter into details, because they would occupy too much space, and I reserve them for a separate work on Centigrade Testing, which I purpose to publish for the use of chemical manufacturers. The specific gravities were determined by weighing the solutions in light bottles, of which three sizes were used, capable of containing respectively 3000, 700, and 350 grs. of water. The balance in which the large bottle was weighed turned with half a grain when loaded. That in which the small bottles were weighed turned with ·01 gr. when loaded. The weighings were all taken when the liquors were at the temperature of 62° F. The greater part of the experiments were made by my assistant, Mr. Joseph White of Nottingham; the others by myself.

The tables of mineral acids were calculated from the experiments already published by Dr. Ure and other chemists.

### *Atomic Volume of Water.*

For the sake of subsequent reference I shall state the atomic volume of water, as derived from the atomic weights both of Dumas and of Berzelius.

TABLE I.—*Water.*

$H^2O$ = 112·48 grs.: Berzelius.
= 112·5 grs.: Dumas.
Temperature 62° Fahrenheit.

| Authorities. | Specific gravity of the liquid. | Grains of $H^2O$ in 1000 septems. | Atoms of $H^2O$ in 1000 septems. | Septems containing 1 atom of $H^2O$. |
|---|---|---|---|---|
| B | 1·000 | 7000·0 | 62·233 | 16·0686 |
| D | 1·000 | 7000·0 | 62·222 | 16·0714 |

The last column of this table shows the *atomic volume of water*, or the bulk of 1 test atom at 62° Fahr., expressed in septems.

## TABLE II.—*Sulphuric Acid.*

$SO^3 = 501{\cdot}165$ grs. Temperature 62° F.

| Authorities for the specific gravity. | Specific gravity of the solution. | Atoms of $SO^3$ in 1000 septems. | Atoms of Water to 1 atom $SO^3$. | 1 $SO^3$ | | Septems of solution containing 1 $SO^3$. |
|---|---|---|---|---|---|---|
| | | | | Occupies: Septems. | Condenses: Septems. | |
| B | 1·97 | 27·516 | 0·0 | 36·34 | 0·0 | 36·343 |
| BM | 1·896 | 23·81 | 0·5 | 33·96 | 2·38 | 41·999 |
| G | 1·848 | 21·081 | 1·0 | 31·37 | 4·97 | 47·437 |
| CU | 1·8484 | 21·00 | 1·02 | 31·19 | 5·15 | 47·619 |
| CU | 1·8393 | 20·00 | 1·27 | 29·63 | 6·71 | 50·000 |
| CU | 1·8212 | 19·00 | 1·51 | 28·37 | 7·97 | 52·632 |
| CU | 1·7961 | 18·00 | 1·75 | 27·37 | 8·97 | 55·556 |
| G | 1·78 | 17·16 | 2·0 | 26·14 | 10·20 | 58·276 |
| CU | 1·7636 | 17·00 | 2·004 | 26·68 | 9·66 | 58·824 |
| CU | 1·7279 | 16·00 | 2·265 | 26·10 | 10·24 | 62·500 |
| CU | 1·6888 | 15·00 | 2·55 | 25·67 | 10·67 | 66·667 |
| CU | 1·6487 | 14·00 | 2·873 | 25·26 | 11·08 | 71·429 |
| G | 1·6321 | 13·623 | 3·0 | 25·19 | 11·15 | 73·403 |
| CU | 1·6086 | 13·00 | 3·245 | 24·78 | 11·56 | 76·923 |
| CU | 1·5672 | 12·00 | 3·67 | 24·33 | 12·01 | 83·333 |
| CU | 1·522 | 11·00 | 4·155 | 24·14 | 12·20 | 90·909 |
| CU | 1·4795 | 10·00 | 4·75 | 23·64 | 12·70 | 100·00 |
| CU | 1·4362 | 9·00 | 5·475 | 23·13 | 13·21 | 111·11 |
| CU | 1·3926 | 8·00 | 6·377 | 22·52 | 13·82 | 125·00 |
| CU | 1·349 | 7·00 | 7·54 | 21·74 | 14·60 | 142·86 |
| CU | 1·3033 | 6·00 | 9·062 | 21·04 | 15·30 | 166·67 |
| CU | 1·2567 | 5·00 | 11·19 | 20·25 | 16·09 | 200·00 |
| CU | 1·2112 | 4·00 | 14·39 | 18·80 | 17·54 | 250·00 |
| CU | 1·1603 | 3·00 | 19·61 | 18·16 | 18·18 | 333·33 |
| CU | 1·1078 | 2·00 | 30·01 | 17·69 | 18·65 | 500·00 |
| CU | 1·088 | 1·60 | 37·86 | 16·59 | 19·75 | 625·00 |
| CU | 1·0567 | 1·00 | 61·30 | 14·89 | 21·45 | 1000·0 |
| CU | 1·0286 | ·50 | 123·6 | 14·21 | 21·13 | 2000·0 |
| CU | 1·0151 | ·25 | 248·2 | 11·20 | 25·14 | 4000·0 |
| CU | 1·0066 | ·10 | 621·9 | 5·59 | 30·75 | 10000· |
| CU | 1·0043 | ·06 | 1037· | − 0·07 | 36·41 | 16667· |
| CU | 1·0037 | ·05 | 1245· | − 2·41 | 38·75 | 20000· |
| CU | 1·0032 | ·04 | 1556· | − 8·40 | 44·74 | 25000· |
| CU | 1·0026 | ·03 | 2075· | −15·07 | 51·41 | 33333· |
| CU | 1·002 | ·02 | 3112· | −28·41 | 64·75 | 50000· |
| CU | 1·0014 | ·01 | 6227· | −68·41 | 104·8 | 100000· |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |

AUTHORITIES.—B = Bussy. The substance is the anhydrous acid = $SO^3$. BM = Bussy for the sp. gr.; Mitscherlich for the chemical constitution. It is the fuming sulphuric acid of Nordhäusen = $SO^3$, $H^2O + SO^3$. G = Graham and Gmelin. CU = my calculations, after the nearest numbers in Ure's table.

### *Description and Plan of* Table II.

I shall give a full description of the table of sulphuric acid to render the plan intelligible, and to enable me to dispense with descriptions of many of the following tables constructed on the same model.

Every horizontal line shows the composition of a decigallon

of solution. Column 2 shows the specific gravity of the solution, or the weight in avoirdupois pounds of a decigallon. By multiplying the specific gravity by 7000, we obtain the weight of a decigallon in grains.

Column 3 shows the absolute weight of anhydrous acid contained in a decigallon of each solution, expressed in test atoms. To find the weight in grains, the numbers in this column must be multiplied by 501·165, the number given at the head of the table as the weight of a test atom.

These two columns of each table contain the physical and chemical data from which all the particulars given in the other columns are derived.

The numbers contained in column 5, which show the "*volume in solution*" occupied by 1 test atom of anhydrous acid at different stages of dilution, are determined by the following calculation. The absolute weight in grains of the anhydrous acid contained in a decigallon of solution is deducted from the absolute weight in grains of the same volume of solution: the difference is the weight in grains of the water. Dividing this difference by 7, we have the volume of the water expressed in septems. Deducting this volume from 1000 (the number of septems contained in a decigallon), the difference shows the number of septems occupied by the known weight of anhydrous acid. Dividing this number of septems by the number of test atoms constituting the known weight of anhydrous acid, the product is the *number of septems occupied by one test atom of the anhydrous acid.* As this calculation is important, I shall illustrate it by two examples.

*First Example.*—Acid of sp. gr. 1·8393, having a chemical strength of 2000°, or 20 test atoms per decigallon.

| | | |
|---|---|---|
| | 1839·3 | = sp. gr. of the solution. |
| Mult. by | 7 | |
| | 12875·1 | = weight of 1000 septems of solution in grs. |
| Deduct | 10023·3 | = weight of 20 test atoms of acid in grs. |
| 7) | 2851·8 | = weight of the water in grs. |
| | 407·4 | = volume of the water in septems. |
| 20) | 592·6 | = volume of the acid in septems. |
| | 29·63 | = volume of 1 test atom of acid in septems. |

*Second Example.*—Acid of sp. gr. 1·0037, chemical strength 5°, or 0·05 test atom per decigallon.

| | | |
|---|---|---|
| | 1003·7 | = sp. gr. of the solution. |
| | 7 | |
| | 7025·9 | = weight of 1000 septems of solution in grs. |
| | 25·058 | = weight of $\frac{1}{20}$th test atom of acid in grs. |
| 7) | 7000·842 | = weight of the water in grs. |
| | 1000·1203 | = volume of the water in septems. |

In this case the water present is in greater quantity than would suffice to *fill* the decigallon measure if water alone was present. The 5° of acid (25·058 grs.) condense their own volume and ·1203 septem besides. The effect produced by 100° of acid, or 1 test atom, is of course 20 times as much, namely, 2·406 septems. I have put this and similar negative quantities in the table with the *minus* sign (−) prefixed to them.

By this calculation we effect a complete analysis of the solution. We begin with—

the volume, the weight } of the solution,
and we find the volume, the weight } of the water,
and the volume, the weight } of the anhydrous acid.

The numbers in column 6, which represent the condensation that takes place, are found by subtracting the numbers contained in column 5 from the number which represents the volume of the test atom of uncombined acid $SO^3$, which number is placed at the head of column 5.

The numbers in column 6 represent the actual condensation effected in each mixture by the chemical power of one test atom of $SO^3$. I do not mean to ascribe the diminution of bulk to the acid, but to the compound which the acid helps to form. There is consequently a fallacy in the statements given in column 5. It is not *absolutely true* that $SO^3$ *occupies* the volume there assigned to it in different solutions. It is only true if the actual condensation that occurs is reckoned solely upon the acid, and none ascribed to the water or the resulting hydrate; but in reality the hydrate alone suffers the whole condensation. This compound has the property of existing, at a given temperature, within a smaller volume than that occupied by its uncombined elements. None of the condensation therefore can be properly ascribed either to the acid or to the water individually. This being understood, the fallacy in the table can lead to no error. The plan adopted has the advantage of rendering the effects of different substances acting on water readily comparable with one another.

The numbers contained in column 7 represent the atomic volume of the different solutions, that is to say, the volume of solution that contains a test atom of the anhydrous acid. To find these numbers we divide 1000 by the numbers contained in column 3, or by the degree expressed in test atoms.

The numbers contained in column 4, which represent the state of hydration expressed in atomic proportions, are deter-

mined by the following process. The numbers in column 7 show the volume in septems of every solution equivalent to 1 test atom of anhydrous acid. Deducting from that number the volume occupied by 1 test atom of anhydrous acid, as quoted in the same horizontal line in column 5, the residue is the quantity of associated water expressed in septems. Dividing this residue by the atomic volume of water, 16·07, the product shows the number of atoms of water that occur in combination with 1 atom of the anhydrous acid.

The range of the experiments recorded in this and the following tables, is from a solution saturated at 62° F. to a solution containing 1° of acid or other substance per decigallon, or 1 test atom in 10 imperial gallons of solution. I do not stop at that stage of dilution because the condensing power of the chemical substances is exhausted, for I find no limit to that power. I stop because experiments performed on liquors further diluted do not give results of sufficient accuracy for this inquiry. It is impossible to determine the exact specific gravity of solutions running between sp. gr. 1·001 and sp. gr. 1·000.

*Observations on some of the prominent features of the Table of Sulphuric Acid.*

Messrs. Playfair and Joule (Memoirs Chem. Soc., vol. ii. p. 428) consider the atomic volume of sulphate of water to be equal to twice the atomic volume of water. Deducting the water, this leaves 16·07 as the volume in solution of the anhydrous sulphuric acid. This agrees with a solution of about 160° of chemical strength, but disaccords with every other solution, weaker or stronger. In fact, anhydrous sulphuric acid has no fixed volume in solution. Its measure extends from + 33·96 septems to −68·41 septems, changing with every change in the composition of its hydrates, so that a single drop of water cannot be added to any solution without diminishing the bulk, by increasing the condensing power, of the anhydrous acid.

The amount of the condensation effected by anhydrous sulphuric acid in its various stages of hydration is remarkable. The atomic volume of the test atom of acid is very nearly 36 septems, or 1 cubic inch. With half an atom, or 8 septems of water, it condenses $2\frac{2}{3}$ septems. With 1 atom, or 16 septems of water, it condenses 5 septems. With 2 atoms, or 32 septems of water, it condenses 10 septems. In all these cases the condensation is equal to nearly one-third part of the entire bulk of the water. With 6227 atoms, or 100105 septems of water, it condenses 105 septems. In this case

the condensation is equal to only one-thousandth part of the bulk of the water, but it is equal to three times the bulk of the uncombined anhydrous acid.

It is curious to compare this chemical condensation with that which is effected in water by simple pressure. A weight of 1 lb. avoirdupois applied to a cube of water of the bulk of 1 septem diminishes its height to the extent of 50 millionths, whereas 1 lb. weight of sulphuric acid, = 14 test atoms, applied to 450 septems of water, = 28 test atoms, occasions a condensation equal to 143 septems, and if applied to 100000 septems of water, it occasions a condensation equal to 1400 septems.

If, as some chemists affirm, dilute solutions are not to be held as chemical compounds, but only as mixtures of acid and water, in what manner shall we account for this enormous condensation? We universally admit, as chemical compounds, the hydrate of sulphuric acid with 1 atom of water (oil of vitriol), and the crystallizable hydrate with 2 atoms of water; but when the compound contains more water than 2 atoms, some of us, for that reason alone, begin to question the occurrence of chemical action. Yet surely the evidence afforded by progressive condensation is not to be disregarded merely because the condensation occurs in a dilute liquor? and if a condensation equal to *ten* septems is taken as a proof of chemical action in the formation of the second hydrate, how can we reasonably declare that a condensation equal to *a hundred* septems, effected by the same quantity of acid, but with more water, is evidence of *no* chemical action?

The rate of condensation does not seem to accord with any arithmetical or geometrical progression. I cannot reduce it to any useful formula. I can perceive no particular relation that it bears to the real specific gravity of the solutions, nor to their chemical strength, nor to the state of hydration of the acid, nor to any other general principle. I am unable to construct a formula with which to determine either the chemical strength of a solution from its specific gravity, or the specific gravity from its chemical strength. But this probably arises from the fact that the subject has not been sufficiently examined; for a glance at the Tables cannot but suggest the opinion, that the condensation effected by every particular substance will have an invariable progression.

In the mean time there is one particular in which we can approach a little towards a knowledge of the laws that regulate specific gravities, and that is, in determining the exact degree in which condensation increases the mean specific gravity of a solution. What I have to say on this head ap-

plies to solutions of all substances, and has therefore a general interest.

If we deduct 1 from the specific gravity of anhydrous sulphuric acid, and divide the residue by the number of test atoms of anhydrous acid that fill a decigallon at 62° F., the product is a fraction, which, when added to 1, represents the mean specific gravity of a solution containing 1 test atom of acid per decigallon. Thus—

$$\frac{\text{sp. gr. } 1{\cdot}97-1}{27{\cdot}516}=\frac{{\cdot}97}{27{\cdot}516}={\cdot}035252.$$

The product $\cdot035252+1=1\cdot035252$ is the mean specific gravity of a solution of acid of 100°.

The same decimal fraction multiplied by any given number, say 20, and then added to 1, gives the mean specific gravity of a solution of the chemical strength indicated by the given number. Thus—

$$({\cdot}035252\times20)+1=1{\cdot}70504,$$

which is the mean specific gravity of a solution of acid of 2000°.

If now we compare the mean specific gravities thus calculated with the real experimental specific gravities of the several solutions, and take the *differences*, we obtain a series of numbers which show the precise extent to which the specific gravities are increased by the condensation resulting from the chemical action of the acid upon the water. I give these differences in the following Table.

TABLE III. Showing the increase of Specific Gravity occasioned in Solutions of $SO^3$ by condensation.

| Degree in atoms. | Increase in spec. grav. | Degree in atoms. | Increase in spec. grav. | Degree in atoms. | Increase in spec. grav. |
|---|---|---|---|---|---|
| 23·81 | ·056650 | 17·00 | ·164316 | 11·00 | ·134228 |
| 21·081 | ·104853 | 16·00 | ·163868 | 10·00 | ·126980 |
| 21·00 | ·108108 | 15·00 | ·160020 | 5·00 | ·080440 |
| 20·00 | ·134260 | 14·00 | ·155172 | 3·00 | ·054544 |
| 19·00 | ·151412 | 13·623 | ·151862 | 1·00 | ·021448 |
| 18·00 | ·161564 | 13·00 | ·150324 | 0·10 | ·003075 |
| 17·16 | ·175076 | 12·00 | ·144176 | 0·01 | ·001048 |

It is commonly stated, in reference to the hydrates of sulphuric acid, that the greatest condensation occurs in the formation of the hydrate $SO^3+3H^2O=1362{\cdot}3°$; but this table shows that the greatest condensation occurs in the formation of the hydrate $SO^3+2H^2O=1716°$. What I mean by the greatest condensation is that which occurs *in a given mass of solution*; for, speaking absolutely, the greatest condensation

effected by 1 atom of $SO^3$ (or of any other substance) is that which occurs when it combines with the largest possible quantity of water. The extent to which this holds true is best seen on examining the specific gravity of a very dilute solution, for example, that of 1°:

1·00000000 = specific gravity of water.
0·00035252 = fraction indicating the mean specific gravity of 1° of acid.
0·00104748 = increase of specific gravity due to condensation.

1·00140000 = real specific gravity of acid of 1°.

The effect produced by condensation is here three times as great as that due to the mere difference of weight between the anhydrous acid and the water which it replaces.

The common attribution of the greatest condensation to the third hydrate is nevertheless true, provided we take the protohydrate as the point of comparison. Thus, 47·437 septems of $SO^3$, $H^2O$ added to 16·07 septems of water = 63·507 septems, whereas the atomic measure of $SO^3 + 2H^2O$ is only 58·276 septems, showing a condensation of 5·231 septems. Again, 47·437 septems of SO, $H^2O$ added to 32·14 septems of water = 79·577 septems, whereas the atomic measure of $SO^3 + 3H^2O$ is 73·403 septems, showing a condensation of 6·174 septems, which exceeds the former condensation by 0·943 septems.

The extent to which the mean specific gravity of a solution is increased by condensation depends necessarily on the actual amount of the condensation. As it is easy to ascertain that amount, it will be proper to point out the exact relation between condensation and the term expressing the real specific gravity of a solution.

If we suppose 500 septems of acid to combine with 500 septems of water, and to condense so much as to form only 999 septems of solution, we shall require 1 septem more of water to fill the standard measure of a decigallon. This adds 7 grs. to the weight of the solution, and therefore increases its specific gravity by ·001. If the condensation is such as to require 5 septems of water to complete the decigallon measure, the weight of the liquor will be increased by 35 grs. and its specific gravity by ·005. For every septem of condensation per decigallon, that is to say, for the condensation of every thousandth part by measure of the solution, the increase in specific gravity will be ·001. This law is universal. The nature of the chemical substance that causes the condensation, the quantity of it contained in the solution, its

specific gravity, its atomic weight, the volume of its anhydrous atom, are all matters of indifference. The sole regulating particular is the extent of condensation per decigallon expressed in septems. *Every septem of condensation per decigallon, effected in any solution, increases the specific gravity by* ·001 (water being = 1·000).

It is easy to test the accuracy of this principle by facts. If we divide the differences given in Table III. by ·001, we find the number of septems that correspond to the condensation per decigallon in each solution. And if the condensation per decigallon is divided by the number of test atoms known to be present in a decigallon of each solution, the product shows the amount of condensation effected by each test atom, and that product corresponds with the number given in column 6 of Table II.

The following calculation, relating to acid of 10 atoms or 1000° of strength, also substantiates this principle.

| | | |
|---|---|---|
| To . . . . . | ·035252 | = fraction indicating the mean specific gravity of 100° of acid, |
| Add . . . . | ·012698 | = condensation per atom in solutions of 1000° of acid: see Table III. |
| | ·047950 | |
| Multiply by | 10 | = number of test atoms of acid per decigallon. |
| Gives . . . | ·479500 | |
| Add . . . . | 1·000000 | = specific gravity of water. |
| Result . . . | 1·479500 | = real specific gravity of acid of 1000°. |

I hold these results to prove that anhydrous sulphuric acid has no fixed atomic volume in solution. There is, nevertheless, a means of indicating the volume of an atom of anhydrous acid in solution, which is free from fallacy, and well-adapted to practical purposes,—I allude to that exhibited in column 7 of Table II. The numbers in this column are all chemically equivalent, and show how many measures of any strong acid must be taken to produce, by dilution with water, the atomic measure of another weaker acid. Thus, 47·437 septems, the atomic measure of $SO^3$, $H^2O$, diluted with water to the bulk of 58·276 septems, produces the hydrate $SO^3$, $2H^2O$; or diluted to the bulk of 73·403 septems, it produces the hydrate $SO^3 + 3H^2O$; or diluted to the bulk of 1000 septems, it produces acid of 100°. The condensation that occurs in these dilutions has been estimated and thrown out, so that we deal only with the practical results. The *atomic measure of a solution* is therefore a definable manageable quantity.

The opinion entertained by Dalton, that anhydrous salts dissolve in water without adding to its bulk, is singularly inapplicable to sulphuric acid. Half an atom of water, measuring 8·035 septems, saturated with $SO^3$, so as to form the fuming acid of 2381°, acquires the volume of 41·999 septems, or 1000 septems of water produce 5227 septems of fuming acid. Thus an anhydrous substance can increase the volume of its solvent water from 8 to 42, or from 1 to $5\frac{1}{4}$, the temperature remaining constant. I shall show, in treating of soda, a result entirely different from this, and yet equally at variance with the hypothesis of Dalton.

The hydrate of sulphuric acid that distils without change in composition is the protohydrate, $SO^3 + H^2O$. Hence the fuming acid, $SO^3, H^2O + SO^3$, cannot be prepared by the concentration of dilute acids.

TABLE IV.—*Muriatic Acid.*

$H^2Cl^2 = 455·13$ grs. Temperature 62° F.

| Authorities for the specific gravity. | Specific gravity of the solution. | Atoms of $H^2Cl^2$ in 1000 septems. | Atoms of water to 1 $H^2Cl^2$. | 1 $H^2Cl^2$. | | Septems of solution containing 1 $H^2Cl^2$. |
|---|---|---|---|---|---|---|
| | | | | Occupies: Septems. | Condenses: Septems. | |
| F | 1·27 | 19·533 | 0·0 | 51·20 | 0·0 | 51·196 |
| G | 1·6963 | 26·089 | 0·0 | 38·33 | 0·0 | 38·350 |
| D | 1·2109 | 7·9021 | 5·49 | 38·33 | ? | 126·55 |
| U | 1·2 | 7·5259 | 5·88 | 38·44 | ? | 132·87 |
| T | 1·203 | 7·5229 | 5·91 | 38·03 | 0·30 | 132·93 |
| B | 1·192 | 7·0216 | 6·52 | 37·68 | 0 65 | 142·42 |
| CU | 1·1891 | 7·00 | 6·53 | 38·00 | 0·33 | 142·86 |
| CU | 1·1662 | 6·00 | 8·05 | 37·32 | 1·01 | 166·67 |
| CU | 1·1408 | 5·00 | 10·15 | 36·86 | 1·47 | 200·00 |
| CU | 1·1148 | 4·00 | 13·3 | 36·32 | 2·01 | 250·00 |
| M | 1·094 | 3·1969 | 17·25 | 35·62 | 2·71 | 312·80 |
| CU | 1·0878 | 3·00 | 18·52 | 35·75 | 2·58 | 333·33 |
| U | 1·0599 | 2·00 | 28·93 | 35·07 | 3·26 | 500·00 |
| CU | 1·0307 | 1·00 | 60·1 | 34·32 | 4·01 | 1000·0 |
| CU | 1·0157 | ·50 | 122·4 | 33·62 | 4·71 | 2000·0 |
| CU | 1·0079 | ·25 | 246·8 | 33·42 | 4·91 | 4000·0 |
| CU | 1·0032 | ·10 | 620 2 | 33·02 | 5·31 | 10000· |
| U | 1·002 | ·06288 | 987· | 33·21 | 5·12 | 15904· |
| CU | 1·0016 | ·05 | 1242· | 33·30 | 5·03 | 20000· |
| CU | 1·0013 | ·04 | 1554· | 32·52 | 5·81 | 25000· |
| CU | 1·001 | ·03 | 2072· | 31·72 | 6·61 | 33333· |
| CU | 1·0006 | ·02 | 3109· | 35·02 | 3·31 | 50000· |
| CU | 1·0003 | ·01 | 6221· | 35·02 | 3·31 | 100000· |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |

AUTHORITIES.—F = Faraday. This line refers to the gaseous acid condensed to the liquid form by the pressure of 40 atmospheres at 50° Fahr. G = Griffin. This line shows the measure of muriatic acid on the supposition that it could exist in an uncombined state at 62° F. and 30 inches Bar. in the same volume that it occupies in the solution of 7·9021, sp. gr. 1·2109. B = Berzelius. D = Davy. M = Mitscherlich, after Dalton. T = Thomson. U = Ure. CU = calculated from the nearest numbers in Ure's table.

*Observations on the Table of Muriatic Acid.*

Muriatic acid has only one-third part of the solubility of sulphuric acid. A saturated solution of the latter contains about 24 test atoms, that of the former only about 8 test atoms per decigallon. The condensing power of muriatic acid is only a tenth part of that of sulphuric acid, and though always progressing with dilution, yet when the acid forms the hydrate containing 6000 atoms of water, where the dilution is about 800 fold, the entire condensation does not amount to 10 septems. The atomic measure at the highest is about $2\frac{1}{3}$ times that of water, and at the lowest is not less than twice that of water.

The limited solubility of certain substances in water has been sometimes ascribed to the action of cohesion, but it is difficult to conceive in what manner cohesion can limit the solubility of muriatic acid gas. The two upper lines in Table IV. exhibit a singular illustration of the effects of cohesion. The compression of 40 atmospheres at 50° F. is required to reduce muriatic acid gas to a liquid of sp. gr. 1·27, in which condition the test atom measures 51·2 septems, and the decigallon contains $19\frac{1}{2}$ test atoms. The compressive power of water acting on the gas at about the same temperature, and under the ordinary pressure of the atmosphere, reduces the anhydrous acid to sp. gr. 1·6963, in which condition its test atom measures only 38·33 septems, and the decigallon contains 26 test atoms. We may judge from this fact that the limited solubility of muriatic acid in water results, not from the cohesion of its particles, but from a quality the very opposite to cohesion.

The fraction which +1 indicates the mean specific gravity of 100° of muriatic acid is (·6963÷26·089=) ·026688.

TABLE V. Showing the increase of Specific Gravity occasioned in Solutions of $H^2Cl^2$ by condensation.

| Atoms of $H^2Cl^2$. | Increase in spec. grav. | Atoms of $H^2Cl^2$. | Increase in spec. grav. | Atoms of $H^2Cl^2$. | Increase in spec. grav. |
|---|---|---|---|---|---|
| 7·00 | ·002284 | 4·00 | ·008048 | 2·00 | ·006524 |
| 6·00 | ·006072 | 3·1969 | ·008680 | 1·00 | ·004012 |
| 5·00 | ·007360 | 3·00 | ·007736 | 0·10 | ·000531 |

The point of greatest condensation in muriatic acid is at that hydrate which distils without alteration in constitution. Mitscherlich (perhaps after Dalton) quotes this hydrate as sp. gr. 1·094, composition = $H^2Cl^2 + 17\frac{1}{4}H^2O$. Professor Clark states the specific gravity to be 1·110, and its composition = $H^2Cl^2 + 16\frac{2}{3}H^2O$. It may possibly be $H^2Cl^2 + 16H^2O$. The hydrate, where the greatest density is united with the

greatest chemical strength, has $5\frac{1}{2}$ atoms of water, or one-third of the quantity which belongs to the hydrate that sustains the greatest amount of condensation.

Messrs. Playfair and Joule (Mem. Chem. Soc. ii. 443, 469, 475) are of opinion that the atomic measure of muriatic acid is, in concentrated solutions, equal to twice the atomic volume of water (p. 469); but that in dilute solutions it is sometimes twice (p. 443) and sometimes only once (pp. 469, 475) the atomic volume of water. They do not specify the point at which they conceive the measure to change suddenly from 2 volumes to 1 volume.

## Table VI.—*Nitric Acid.*

$N^2O^5 = 677{\cdot}036$ grs. Temperature 62° F.

| Authorities for the specific gravity. | Specific gravity of the solution. | Atoms of $N^2O^5$ in 1000 septems. | Atoms of water to 1 $N^2O^5$. | 1 $N^2O^5$ | | Septems of solution containing 1 $N^2O^5$. |
|---|---|---|---|---|---|---|
| | | | | Occupies: Septems. | Condenses: Septems. | |
| $N^2O^5$ | 1·6651 | 17·216 | 0·0 | 58·09 | 0·0 | 58·087 |
| G | 1·521 | 13·485 | 1·0 | 58·09 | ? | 74·154 |
| CU | 1·5091 | 13·00 | 1·2 | 57·56 | 0·53 | 76·923 |
| CU | 1·4948 | 12·00 | 1·73 | 55·49 | 2·60 | 83·333 |
| G | 1·485 | 11·524 | 2·0 | 54·64 | 3·45 | 86·772 |
| CU | 1·4746 | 11·00 | 2·32 | 53·57 | 4·52 | 90·909 |
| CU | 1·452 | 10·019 | 3·0 | 51·60 | 6·49 | 99·812 |
| CU | 1·4518 | 10·00 | 3·01 | 51·54 | 6·55 | 100·00 |
| CU | 1·4256 | 9·00 | 3·84 | 49·43 | 8·66 | 111·11 |
| G | 1·42 | 8·8203 | 4·0 | 49·10 | 8·99 | 113·37 |
| CU | 1·3962 | 8·00 | 4·84 | 47·19 | 10·90 | 125·00 |
| CU | 1·4 | 7·9069 | 5·0 | 46·13 | 11·96 | 126·47 |
| CU | 1·3602 | 7·00 | 6·07 | 45·26 | 12·83 | 142·86 |
| CU | 1·322 | 6·00 | 7·69 | 43·05 | 15·04 | 166·67 |
| T | 1·322 | 5·8579 | 8·0 | 42·16 | 15·93 | 170·71 |
| CU | 1·2792 | 5·00 | 9·9 | 40·88 | 17·21 | 200·00 |
| T | 1·2844 | 4·9799 | 10·0 | 40·12 | 17·97 | 200·81 |
| CU | 1·2305 | 4·00 | 13·12 | 39·09 | 19·00 | 250·00 |
| T | 1·2012 | 3·5484 | 15·0 | 40·78 | 17·31 | 281·82 |
| CU | 1·1766 | 3·00 | 18·39 | 37·85 | 20·24 | 333·33 |
| CU | 1·1207 | 2·00 | 28·85 | 36·37 | 21·72 | 500·00 |
| CU | 1·0619 | 1·00 | 60·06 | 34·82 | 23·27 | 1000·0 |
| CU | 1·0314 | ·50 | 122·3 | 33·92 | 24·17 | 2000·0 |
| CU | 1·0158 | ·25 | 246·8 | 33·52 | 24·57 | 4000·0 |
| CU | 1·0064 | ·10 | 620·2 | 32·72 | 25·37 | 10000· |
| CU | 1·0032 | ·05 | 1242· | 32·72 | 25·37 | 20000· |
| CU | 1·0026 | ·04 | 1554· | 31·71 | 26·38 | 25000· |
| CU | 1·002 | ·03 | 2072· | 30·05 | 28·04 | 33333· |
| CU | 1·0013 | ·02 | 3109· | 31·72 | 26·37 | 50000· |
| CU | 1·0007 | ·01 | 6221· | 26·72 | 31·37 | 100000· |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |

Authorities.—G = Graham. T = Thomson. CU = Calculated after the nearest numbers in Ure's table. The specific gravity of the anhydrous acid is calculated on the supposition that it could exist in a free state at 62° F., under the same volume that it occupies in the protohydrate.

*Observations on the Table of Nitric Acid.*

The greatest chemical strength of nitric acid in solution is $1348\frac{1}{2}^{\circ}$. This constitutes the protohydrate of sp. gr. 1·521. The volume of a test atom of acid, as it exists in this hydrate, is 58·09 septems. The condensation which occurs in diluted solutions extends to 31 septems per test atom in a solution of 1°, where the dilution is 1348 fold. Both as respects solubility and power of condensation, nitric acid stands between sulphuric acid and muriatic acid.

The fraction which + 1 indicates the mean specific gravity of 100° of nitric acid is (·6651 ÷ 17·216 =) ·038634.

TABLE VII. Showing the increase of Specific Gravity occasioned in Solutions of $N^2O^5$ by condensation.

| Atoms of $N^2O^5$. | Increase in spec. grav. | Atoms of $N^2O^5$. | Increase in spec. grav. | Atoms of $N^2O^5$. | Increase in spec. grav. |
|---|---|---|---|---|---|
| 13·00 | ·006858 | 8·8203 | ·079228 | 4·00 | ·075964 |
| 12·00 | ·031192 | 8·00 | ·087128 | 3·00 | ·060698 |
| 11·00 | ·049626 | 7·00 | ·089762 | 2·00 | ·043432 |
| 10·00 | ·065460 | 6·00 | ·090196 | 1·00 | ·023266 |
| 9·00 | ·077894 | 5·00 | ·086030 | 0·01 | ·000314 |

The point of greatest density in the hydrates of nitric acid coincides with that of greatest chemical strength, namely, in the protohydrate. The hydrate that distils without alteration in constitution is $N^2O^5, 4H^2O$. The hydrate that sustains the greatest amount of condensation is $N^2O^5, 8H^2O$.

Messrs. Playfair and Joule's account of the atomic volume of nitric acid is as follows (Mem. Chem. Soc. vol. ii. p. 469): —"Nitrate of water in the acid of sp. gr. 1·42 seems to affect four volumes. . . . . Nitrate of water calculated on weak acids has three volumes; but there being no good fixed point upon which to make the calculation, we must leave at present this point undetermined."

This estimate of the atomic measure of the acid in solution of sp. gr. 1·42 is nearly correct. Four volumes for the hydrate is three volumes for the anhydrous acid, and 3 × 16·07 = 48·21, while the number given in Table VI. is 49·10 septems. Three volumes is also correct for the hydrate in a *single* weak solution; for 16·07 × 2 = 32·14 septems is nearly the atomic measure of the anhydrous acid in a solution of $4^{\circ}$. But there is no sudden fall in the atomic volume from 4 to 3, nor do these numbers apply to any solutions save the two that are named specially. They are only separate links of a long chain, whose parts are all of different magnitudes.

## TABLE VIII.—*Acetic Acid.*

$C^4 H^6 O^3 = 643{\cdot}19$ grs. Temperature 62° F.

| Specific gravity of the solution. | Atoms of $C^4 H^6 O^3$ in 1000 septems. | Atoms of water to 1 $C^4 H^6 O^3$. | 1 $C^4 H^6 O^3$ | | Septems of solution containing 1 $C^4 H^6 O^3$. |
|---|---|---|---|---|---|
| | | | Occupies: Septems. | Condenses: Septems. | |
| 1·067645 | 11·62 | 0·0 | 86·06 | | 86·063 |
| 1·057 | 9·79 | 1·000 | 86·06 | ? | 102·14 |
| 1·058286 | 9·55 | 1·178 | 85·78 | 0·28 | 104·71 |
| 1·068800 | 9·00 | 1·672 | 84·24 | 1·82 | 111·11 |
| 1·068857 | 9·00 | 1·673 | 84·23 | 1·83 | 111·11 |
| 1·071043 | 8·50 | 2·124 | 83·52 | 2·54 | 117·65 |
| 1·073657 | 8·20 | 2·430 | 82·90 | 3·16 | 121·95 |
| 1·074428 | 8·00 | 2·640 | 82·58 | 3·48 | 125·00 |
| 1·073971 | 7·50 | 3·193 | 82·02 | 4·04 | 133·33 |
| 1·073286 | 7·00 | 3·823 | 81·42 | 4·64 | 142·86 |
| 1·069029 | 6·00 | 5·370 | 80·38 | 5·68 | 166·67 |
| 1·063800 | 5·00 | 7·521 | 79·12 | 6·94 | 200·00 |
| 1·056386 | 4·00 | 10·72 | 77·79 | 8·27 | 250·00 |
| 1·044043 | 3·00 | 15·94 | 77·20 | 8·86 | 333·33 |
| 1·031514 | 2·00 | 26·38 | 76·13 | 9·93 | 500·00 |
| 1·016343 | 1·00 | 57·53 | 75·54 | 10·52 | 1000·0 |
| 1·015029 | ·90 | 64·46 | 75·19 | 10·87 | 1111·1 |
| 1·013714 | ·80 | 73·13 | 74·74 | 11·32 | 1250·0 |
| 1·012114 | ·70 | 84·26 | 74·58 | 11·48 | 1428·6 |
| 1·010314 | ·60 | 99·07 | 74·69 | 11·37 | 1666·7 |
| 1·008629 | ·50 | 119·8 | 74·63 | 11·43 | 2000·0 |
| 1·007057 | ·40 | 150·9 | 74·24 | 11·82 | 2500·0 |
| 1·005029 | ·30 | 202·7 | 75·12 | 10·94 | 3333·3 |
| 1·003429 | ·20 | 306·5 | 74·74 | 11·32 | 5000·0 |
| 1·002743 | ·15 | 410·3 | 73·60 | 12·46 | 6666·7 |
| 1·001943 | ·10 | 617·8 | 72·46 | 13·60 | 10000· |
| 1·001771 | ·09 | 686·9 | 72·20 | 13·86 | 11111· |
| 1·001600 | ·08 | 773·4 | 71·88 | 14·18 | 12500· |
| 1·001457 | ·07 | 884·6 | 71·07 | 14·99 | 14286· |
| 1·001286 | ·06 | 1033· | 70·46 | 15·60 | 16667· |
| 1·001129 | ·05 | 1240· | 69·31 | 16·75 | 20000· |
| 1·000914 | ·04 | 1551· | 69·03 | 17·03 | 25000· |
| 1·000700 | ·03 | 2070· | 68·55 | 17·51 | 33333· |
| 1·000529 | ·02 | 3107· | 65·46 | 20·60 | 50000· |
| 1·000286 | ·01 | 6219· | 63·31 | 22·75 | 100000· |
| 2 | 3 | 4 | 5 | 6 | 7 |

### *Observations on the Table of Acetic Acid.*

The whole of this table, with the exception of the first two lines, is calculated from my experiments. The acid on which the experiments were made was prepared for me by Mr. Charles Glassford, chemist to Messrs. Turnbull and Co., Camlachie. It was very pure.

Upon crystallizing a quantity of this acid and pouring off the mother-liquor, I found the latter to have a strength of 910°. The crystals were melted, the solution recrystallized, the crystals pounded, the mother-liquor drained off, the cry-

stals remelted, recrystallized, abstracted once more from the mother-liquor, and finally brought into solution in a closed bottle at 62° F., and not heated higher than that point. The specific gravity of the solution thus procured was 1·058286, and its chemical strength 955°, which gives the formula $C^4 H^6 O^3 + 1{\cdot}178\ H^2 O$, showing nearly one-fifth part of an atom more water than belongs to the protohydrate. Repeated trials brought me no nearer to the protohydrate, which I imagine is partly owing to the difficulty of separating the mother-liquor entirely from the crystals. Van der Toorn (Report of the Fourth Meeting of the British Association, Edin. 1834) states the specific gravity of the protohydrate at 59° F. to be 1·057, which makes its strength to be 979°. This is possibly correct, and I have inserted it in the Table, in company with the specific gravity of the anhydrous acid, calculated from Van der Toorn's number. Of course the anhydrous acid is hypothetical.

The weaker solutions of acetic acid were prepared by dilution of the strong acid in stoppered graduated glass cylinders. The quantity of acid contained in each diluted solution was determined by neutralization with weak ammonia of known strength, applied by means of a pouret; the mixing being effected in a stoppered glass bottle, and solution of litmus being employed to test the point of neutralization. All the adjustments, measurements and weighings were effected at 62° F.

The fraction which + 1 indicates the mean specific gravity of 100° of acetic acid is (·067645 ÷ 11·6194 =) ·005822.

TABLE IX. Showing the increase of Specific Gravity occasioned in Solutions of $C^4 H^6 O^3$ by condensation.

| Atoms of $C^4 H^6 O^3$. | Increase in spec. grav. | Atoms of $C^4 H^6 O^3$. | Increase in spec. grav. | Atoms of $C^4 H^6 O^3$. | Increase in spec. grav. |
|---|---|---|---|---|---|
| 9·55 | ·002686 | 6·00 | ·034097 | 2·00 | ·019870 |
| 9·00 | ·016402 | 5·00 | ·034690 | 1·00 | ·010521 |
| 8·00 | ·027852 | 4·00 | ·033098 | 0·10 | ·001361 |
| 7·00 | ·032532 | 3·00 | ·026577 | 0·01 | ·000228 |

In acetic acid, the greatest chemical strength, the greatest density and the greatest condensation characterize three different hydrates. None of the mineral acids possess this singular divergence of properties. The greatest chemical strength is the property of the protohydrate of 979° (Van der Toorn), or according to my experiments at 62° F., of the solution of 955°. The greatest density is at about 800°, where the hydrate has nearly 3 atoms of water. The greatest condensation

occurs at about 500°, where the hydrate has about $7\frac{1}{2}$ atoms of water.

The measure of the test atom of acetic acid is 86·06 septems. It is therefore much larger than the measure of any of the mineral acids, while its specific gravity is greatly below that of any of them. The peculiarities of acetic acid depend upon these two properties.

Acetic acid of 979° has a specific gravity of 1·057. The addition of as much water as reduces its strength to 800° increases its specific gravity to 1·074428. The addition of as much more water as reduces its strength to 400° brings down its specific gravity to 1·056386, which is nearly the same as the specific gravity of the strongest solution of 979°. These singular properties admit of a simple explanation.

The density of anhydrous acetic acid being not much greater than that of water, little change in the specific gravity of its solutions is produced by simply replacing a proportion of one constituent by the other; yet, if no condensation occurred, the density of all the solutions would no doubt run in regular progression from the density of the strongest acid, 1·057, to the density of water, 1·000. But in fact, the specific gravity rises from 1·057 to nearly 1·075, and then descends towards 1·000. This irregularity results entirely from the condensation that occurs in the formation of the series of hydrates. So great is this condensation, in proportion to the density of the acid, that many of the hydrates are rendered by it not only denser than the protohydrate, but denser than even the anhydrous acid itself. The mean density of acid of 800° is 1·046576 [=(·005822 × 8)+ 1]. When we add to this the effect of condensation, which is ·027852 (=3·4815 × 8), we obtain the actual specific gravity of the solution, 1·074428. The mean density of acid of 500° is 1·029110 [=(·005822 × 5)+1], which, added to the density occasioned by condensation, ·034690 (= 6·94 × 5), gives the real specific gravity of acid of that strength, 1·063800. Hence the laws which regulate the specific gravities of solutions rule in the same way over acetic acid that they do over sulphuric acid. The singular rise and fall in the specific gravity of solutions of acetic acid are due to the existence of no extraordinary property in that acid, but to the regular operation of a simple universal principle that acts alike upon all substances whatever.

Dalton's hypothesis, that organic substances on being dissolved in water increase its bulk only by the amount of water pre-existing in them, or by the oxygen and hydrogen which they contain, is at variance with the properties of an-

hydrous acetic acid. According to that hypothesis, the measure of the test atom of this acid in solution should be equal to that of 3 atoms of water = 48·21 septems (= 16·07 × 3), whereas the measure actually varies in different solutions from 86·06 septems to 63·31 septems. It follows, that Dalton's hypothesis can never be used in the analytical examination of organic substances of unknown composition.

TABLE X.—*Anhydrous Potash.*

KO = 589·916 grs. Temperature 62° F.

| Specific gravity of the solution. | Atoms of KO in 1000 septems. | Atoms of water to 1 KO. | 1 KO | | Septems of solution containing 1 KO. |
|---|---|---|---|---|---|
| | | | Occupies: septems. | Condenses: septems. | |
| 2·656 K. | 31·516 | 0·0 | 31·73 | 0·0 | 31·730 |
| 2·1 D. | 20·928 | 1·0 | 31·73 | 0·0 | 47·782 |
| 1·5607 | 8·10 | 6·75 | 15·05 | 16·68 | 123·46 |
| 1·5594 | 8·00 | 6·89 | 14·35 | 17·38 | 125·00 |
| 1·4909 | 7·00 | 8·01 | 14·14 | 17·59 | 142·86 |
| 1·4374 | 6·00 | 9·66 | 11·37 | 20·36 | 166·67 |
| 1·371 | 5·00 | 11·82 | 10·07 | 21·66 | 200·00 |
| 1·3161 | 4·00 | 15·23 | 5·25 | 26·48 | 250·00 |
| 1·2508 | 3·0835 | 20·00 | 2·94 | 28·79 | 324·31 |
| 1·2446 | 3·00 | 20·15 | 2·74 | 28·99 | 333·33 |
| 1·1815 | 2·0862 | 30·00 | − 2·73 | 34·46 | 479·33 |
| 1·176 | 2·00 | 31·35 | − 3·73 | 35·46 | 500·00 |
| 1·0929 | 1·00 | 62·77 | − 8·63 | 40·36 | 1000·0 |
| 1·0471 | ·50 | 125·1 | − 9·92 | 41·65 | 2000·0 |
| 1·026 | ·25 | 250·1 | −19·72 | 51·45 | 4000·0 |
| 1·0114 | ·10 | 624·2 | −30·72 | 62·45 | 10000· |
| 1·0116 | ·10 | 624·2 | −31·73 | 63·46 | 10000· |
| 1·0078 | ·06 | 1040· | −45·49 | 77·22 | 16667· |
| 1·007 | ·05 | 1248· | −55·72 | 87·45 | 20000· |
| 1·00486 | ·04 | 1556· | −37·15 | 68·88 | 25000· |
| 1·00403 | ·03 | 2077· | −50·01 | 81·74 | 33333· |
| 1·00293 | ·02 | 3155· | −62·16 | 93·89 | 50000· |
| 1·00146 | ·01 | 6227· | −61·44 | 93·17 | 100000· |
| 2 | 3 | 4 | 5 | 6 | 7 |

AUTHORITIES.—D = Dalton. The substance is solid caustic potash. K = Karsten. The substance is anhydrous potash. The solutions are all calculated from my experiments.

*Observations on the Table of Anhydrous Potash.*

The strongest solution of potash that I could prepare at the temperature of 62° F. had the sp. gr. of 1·5607. Its chemical strength was 810°. This was determined by neutralization with pure sulphuric acid of 100°. Its formula is KO, $6\frac{3}{4}H^2O$. According to Karsten the specific gravity of anhydrous potash is *about* 2·656, which gives 31·73 septems for the volume of the test atom; but Dalton's specific gravity

of the hydrate of potash gives the very same number for the volume of anhydrous potash. As it is improbable that potash and water would combine to form the first hydrate without condensation, I conclude that Karsten has merely calculated the specific gravity of anhydrous potash from the specific gravity of the hydrate.

The condensation effected by potash is considerable, nearly approaching to that effected by sulphuric acid. In a solution of 1° the condensation per atom is 93 septems, being three times the measure of the anhydrous potash which causes it.

The fraction which + 1 indicates the mean specific gravity of 100° of potash is (1·656÷31·516=) ·052545.

TABLE XI. Showing the increase of Specific Gravity occasioned in Solutions of KO by condensation.

| Atoms of KO. | Increase in spec. grav. | Atoms of KO. | Increase in spec. grav. | Atoms of KO. | Increase in spec. grav. |
|---|---|---|---|---|---|
| 8·10 | ·135086 | 6·00 | ·122130 | 3·00 | ·086965 |
| 8·00 | ·139040 | 5·00 | ·108275 | 2·00 | ·070910 |
| 7·00 | ·123085 | 4·00 | ·106520 | 1·00 | ·040355 |

The greatest chemical strength, the greatest density, and the greatest condensation in solutions of potash, all coincide. In this particular potash agrees with soda, and with the two fixed alkaline carbonates, but disagrees with the four acids. The above table shows indeed rather more condensation in a solution of 800° than in a solution of 810°, but the difference falls within the limits of errors of experiment. It is difficult to determine the specific gravity of a solution of potash saturated at 62° F., because in cooling down a hot saturated solution an abundant crystallization occurs at about 64° F., which raises the temperature to above 70° F. If the solution is not well-shaken, an excess of potash remains in it at 62° F. If the temperature is allowed to descend a little lower than 62° F., too much potash precipitates. The saturated solutions of caustic soda, carbonate of soda, and carbonate of potash possess similar properties. All these substances crystallize with facility when in saturated solutions at 62° F. It is therefore very difficult to determine the point of saturation.

TABLE XII.—*Carbonate of Potash.*

$KO,CO^2$=886·354 grs. Temperature 62° F.

| Specific gravity of the solution. | Atoms of $KO,CO^2$ in 1000 septems. | Atoms of water to 1 $KO,CO^2$. | 1 $KO,CO^2$ | | Septems of solution containing 1 $KO,CO^2$. |
|---|---|---|---|---|---|
| | | | Occupies: septems. | Condenses: septems. | |
| 2·2643 | 18·295 | 0·0 | 54·66 | 0·0 | 54·660 |
| 1·5739 | 6·65 | 7·03 | 37·46 | 17·20 | 150·48 |
| 1·5248 | 6·00 | 8· | 36·30 | 18·36 | 166·67 |
| 1·459 | 5·1292 | 10· | 34·28 | 20·38 | 194·96 |
| 1·4489 | 5·00 | 10·33 | 33·99 | 20·67 | 200·00 |
| 1·3681 | 4·00 | 13·62 | 31·02 | 23·64 | 250·00 |
| 1·2871 | 3·00 | 19· | 28·07 | 26·59 | 333·33 |
| 1·2753 | 2·865 | 20· | 27·67 | 26·99 | 349·04 |
| 1·2426 | 2·50 | 23·23 | 26·72 | 27·94 | 400·00 |
| 1·2011 | 2·00 | 29·67 | 23·21 | 31·45 | 500·00 |
| 1·1995 | 1·98 | 30· | 23·00 | 31·66 | 505·06 |
| 1·1047 | 1·00 | 61·05 | 19·06 | 35·60 | 1000·0 |
| 1·05509 | ·50 | 123·4 | 13·59 | 41·07 | 2000·0 |
| 1·05517 | ·50 | 123·4 | 13·42 | 41·24 | 2000·0 |
| 1·05529 | ·50 | 123·6 | 13·19 | 41·47 | 2000·0 |
| 1·04466 | ·40 | 154·8 | 12·12 | 42·54 | 2500·0 |
| 1·0284 | ·25 | 248·3 | 10·17 | 44·49 | 4000·0 |
| 1·02829 | ·25 | 248·2 | 10·62 | 44·04 | 4000·0 |
| 1·02203 | ·20 | 310·3 | 13·62 | 41·04 | 5000·0 |
| 1·023 | ·20 | 310·4 | 8·77 | 45·89 | 5000·0 |
| 1·02386 | ·20 | 310·8 | 4·48 | 50·18 | 5000·0 |
| 1·01251 | ·10 | 622·3 | − 1·38 | 56·04 | 10000· |
| 1·01257 | ·10 | 622·4 | − 2·52 | 57·18 | 10000· |
| 1·01271 | ·10 | 622·5 | − 3·38 | 58·04 | 10000· |
| 1·00749 | ·06 | 1037· | − 1·00 | 55·66 | 16667· |
| 1·00631 | ·05 | 1245· | − 2·57 | 57·23 | 20000· |
| 1·005 | ·04 | 1556· | − 1·24 | 55·90 | 25000· |
| 1·00417 | ·03 | 2075· | −15·28 | 69·94 | 33333· |
| 1·00297 | ·02 | 3113· | −24·81 | 79·47 | 50000· |
| 1·00143 | ·01 | 6224· | −19·09 | 73·75 | 100000· |
| 1·00146 | ·01 | 6224· | −21·95 | 76·61 | 100000· |
| 1·00151 | ·01 | 6224· | −27·66 | 82·32 | 100000· |
| 2 | 3 | 4 | 5 | 6 | 7 |

AUTHORITIES.—The specific gravity of the anhydrous salt is quoted from Karsten. The rest of this Table is from my own experiments.

*Observations on the Table of Carbonate of Potash.*

The strongest solution of carbonate of potash that can be formed at 62° F. has a specific gravity of 1·5739 and a chemical strength of 665°. Its formula is $KO,CO^2 + 7H^2O$. The greatest amount of condensation occurs in this first solution, where the measure of the test atom of carbonate of potash decreases at once from 54·66 septems to 37·46 septems, effecting a condensation of 17·20 septems. In a solution of

1° the atomic measure is diminished to −27·66 septems, the condensation effected by 1 test atom being 82·32 septems.

According to Messrs. Playfair and Joule (Mem. Chem. Soc., vol. ii. p. 454), the atomic measure of carbonate of potash in solution is equal to that of water [namely, 16·07 septems]. This is correct when the strength of the solution is about 70°, but not under any other circumstances; since at 400° the measure is twice as much, at 10° the measure is nothing, at 3° it is minus one volume, and at 1° it is minus two volumes.

The fraction which + 1 indicates the mean specific gravity of 100° of carbonate of potash is (1·2643÷18·295=) ·069106.

## TABLE XIII.—*Anhydrous Soda.*

NaO=390·897 grs. Temperature 62° F.

| Authorities for the specific gravity. | Specific gravity of the solution. | Atoms of NaO in 1000 septems. | Atoms of water to 1 NaO. | 1 NaO. | | Septems of solution containing 1 NaO. |
|---|---|---|---|---|---|---|
| | | | | Occupies: septems. | Condenses: septems. | |
| K | 2·805 | 50·231 | 0·0 | 19·91 | 0·0 | 19·908 |
| D | 2·0 | 27·812 | 1·0 | 19·89 | 0·02 | 35·955 |
| G | 1·4 | 7·00 | 8·972 | − 1·30 | 21·21 | 142·86 |
| CT | 1·36 | 6·2809 | 10· | − 1·47 | 21·38 | 159·21 |
| CT | 1·3508 | 6·00 | 10·53 | − 2·62 | 22·53 | 166·67 |
| CT | 1·3076 | 5·00 | 12·8 | − 5·68 | 25·59 | 200·00 |
| CT | 1·2655 | 4·00 | 16·21 | −10·53 | 30·44 | 250·00 |
| CT | 1·2335 | 3·27 | 20· | −15·56 | 35·47 | 305·81 |
| CT | 1·2153 | 3·00 | 21·73 | −15·92 | 35·83 | 333·33 |
| CT | 1·1546 | 2·1465 | 30· | −16·18 | 36·09 | 465·88 |
| CT | 1·1443 | 2·00 | 32·13 | −16·31 | 36·22 | 500·00 |
| G | 1·0727 | 1·00 | 63·28 | −16·86 | 36·77 | 1000·0 |
| G | 1·0554 | ·70 | 90·06 | −18·64 | 38·55 | 1428·6 |
| G | 1·0478 | ·60 | 105·2 | −23·82 | 43·73 | 1666·7 |
| G | 1·0482 | ·60 | 105·2 | −24·54 | 44 45 | 1666·7 |
| G | 1·039 | ·50 | 125·8 | −22·16 | 42·07 | 2000·0 |
| G | 1·0412 | ·50 | 126·0 | −25·56 | 45·47 | 2000·0 |
| G | 1·0207 | ·25 | 250·6 | −26·96 | 46·87 | 4000·0 |
| G | 1·009 | ·10 | 624·4 | −34·16 | 54·07 | 10000· |
| G | 1·0047 | ·06 | 1039· | −22·73 | 42·64 | 16667· |
| G | 1·0052 | ·06 | 1039· | −31·30 | 51·21 | 16667· |
| G | 1·004 | ·05 | 1246· | −24·16 | 44·07 | 20000· |
| G | 1·0043 | ·05 | 1247· | −31·02 | 50·93 | 20000· |
| G | 1·0033 | ·04 | 1557· | −26·30 | 46·21 | 25000· |
| G | 1·0022 | ·03 | 2075· | −15·59 | 35·50 | 33333· |
| G | 1·0018 | ·02 | 3114· | −37·02 | 56·93 | 50000· |
| G | 1·00203 | ·02 | 3114· | −45·58 | 65·49 | 50000· |
| G | 1·0009 | ·01 | 6226· | −29·90 | 49·81 | 100000· |
| G | 1·00106 | ·01 | 6226· | −49·87 | 69·78 | 100000· |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |

AUTHORITIES.—D = Dalton. G = Griffin. K = Karsten. CT = calculated after the nearest numbers in Tünnerman's table.

*Observations on the Table of Anhydrous Soda.*

The strongest solution of anhydrous soda, prepared at 62° F., has a chemical strength of 700° and a density of 1·4. Its formula is $NaO + 9H^2O$. The greatest condensation occurs in this solution, where the test atom of soda effects at once a condensation exceeding its own volume. The atomic measure of the uncombined soda is 19·91 septems, and that of the soda in the strongest solution is −1·30 septem. Hence a decigallon of this solution contains seven times 391 grs. of anhydrous soda, in addition to more water than would fill the vessel if no soda was present. It is impossible to obtain any solution of soda at 62° F., a decigallon of which does not contain more than a decigallon of water. I have already noticed the fact, that 1000 septems of water, when saturated with anhydrous sulphuric acid, produce 5227 septems of solution. By way of contrast, I may state that 1000 septems of water, when saturated with 140 septems of anhydrous soda, produce only 991 septems of solution; and yet the condensation effected by 1 test atom of soda in a solution of this kind, is only one-third part of that which it effects in a solution of 1°. At that stage of dilution the condensation effected by 140 septems of anhydrous soda amounts to about 400 septems.

The fraction which +1 indicates the mean specific gravity of 100° of soda is (1·805 ÷ 50·231 =) ·035934.

The specific gravity of the saturated solution of 700° or specific gravity 1·4 may be explained thus:—

1·000000 = specific gravity of water.
·251538 = ·035934 × 7 atoms, for mean specific gravity.
·148470 = 21·21 × 7 atoms, for effects of condensation.

1·400008 = real specific gravity of solution of 700°.

In a solution of 300° the density caused by condensation *equals* that which is produced by the replacement of water by the anhydrous alkali, and in weaker solutions the density induced by condensation is *much greater* than that occasioned by the replacement of water by alkali, although the uncombined alkali possesses nearly three times the density of water.

When a test atom of caustic soda dissolves in a minimum of water (say 9 test atoms), the condensation it effects is 21 septems; but when it dissolves in a maximum of water (say 6226 test atoms), the condensation effected is three times as much. Those chemists who consider that hydrate of soda dissolves in water without combining with it chemically, will, it appears to me, not easily account for this condensation.

## TABLE XIV.—*Carbonate of Soda.*

### $NaO, CO^2 = 667{\cdot}335$ grs. Temperature 60° F.

| Specific gravity of the solution. | Atoms of $NaO, CO^2$ in 1000 septems. | Atoms of water to 1 $NaO, CO^2$. | 1 $NaO, CO^2$ | | Septems of solution containing 1 $NaO, CO^2$. |
|---|---|---|---|---|---|
| | | | Occupies: septems. | Condenses: septems. | |
| 2·4659 | 25·866 | 0·0 | 38·66 | 0·0 | 38·661 |
| 1·51 | 6·7446 | 8·0 | 19·72 | 18·94 | 148·27 |
| 1·423 | 5·5582 | 10·0 | 19·23 | 19·43 | 179·91 |
| 1·166 | 1·85 | 33·29 | 5·60 | 33·06 | 540·54 |
| 1·15643 | 1·80 | 34·05 | 8·43 | 30·23 | 555·55 |
| 1·156 | 1·79 | 34·25 | 8·18 | 30·48 | 558·66 |
| 1·13971 | 1·60 | 38·39 | 8·01 | 30·65 | 625·00 |
| 1·141 | 1·60 | 38·44 | 7·20 | 31·46 | 625·00 |
| 1·13571 | 1·50 | 41·18 | 4·86 | 33·80 | 666·67 |
| 1·12229 | 1·40 | 43·95 | 7·98 | 30·68 | 714·29 |
| 1·10971 | 1·20 | 51·61 | 3·90 | 34·76 | 833·33 |
| 1·11029 | 1·20 | 51·64 | 3·40 | 35·26 | 833·33 |
| 1·0939 | 1·00 | 62·14 | 1·45 | 37·21 | 1000·0 |
| 1·094 | 1·00 | 62·15 | 1·33 | 37·33 | 1000·0 |
| 1·07729 | ·80 | 77·86 | − 1·27 | 39·93 | 1250·0 |
| 1·05806 | ·60 | 103·8 | − 1·43 | 40·09 | 1666·7 |
| 1·05817 | ·60 | 103·8 | − 1·62 | 40·28 | 1666·7 |
| 1·04929 | ·50 | 124·6 | − 3·24 | 41·90 | 2000·0 |
| 1·0494 | ·50 | 124·7 | − 3·75 | 42·41 | 2000·0 |
| 1·0384 | ·40 | 155·6 | − 0·67 | 39·33 | 2500·0 |
| 1·03843 | ·40 | 155·6 | − 0·74 | 39·40 | 2500·0 |
| 1·03066 | ·30 | 207·8 | − 6·86 | 45·52 | 3333·3 |
| 1·02589 | ·25 | 249·4 | − 8·21 | 46·87 | 4000·0 |
| 1·02117 | ·20 | 311·8 | −10·52 | 49·18 | 5000·0 |
| 1·01157 | ·10 | 623·5 | −20·38 | 59·04 | 10000·0 |
| 1·01163 | ·10 | 623·6 | −20·95 | 59·61 | 10000·0 |
| 1·0119 | ·10 | 623·7 | −23·52 | 62·18 | 10000· |
| 1·00671 | ·06 | 1038· | −16·57 | 55·23 | 16667· |
| 1·00674 | ·06 | 1038· | −17·05 | 55·71 | 16667· |
| 1·00526 | ·05 | 1245· | − 9·81 | 48·47 | 20000· |
| 1·00571 | ·05 | 1246· | −18·95 | 57·61 | 20000· |
| 1·00409 | ·04 | 1556· | − 6·81 | 45·47 | 25000· |
| 1·00457 | ·04 | 1557· | −18·95 | 57·61 | 25000· |
| 1·00343 | ·03 | 2075· | −18·97 | 57·63 | 33333· |
| 1·00349 | ·03 | 2076· | −20·86 | 59·52 | 33333· |
| 1·00274 | ·02 | 3114· | −41·80 | 80·46 | 50000· |
| 1·0028 | ·02 | 3114· | −44·66 | 83·32 | 50000· |
| 1·0016 | ·01 | 6227· | −64·67 | 103·33 | 100000· |
| 1·00166 | ·01 | 6227· | −70·38 | 109·04 | 100000· |
| 2 | 3 | 4 | 5 | 6 | 7 |

The three substances at the head of the list are solids. 2·4659 is the specific gravity of anhydrous carbonate of soda, as given by Karsten. 1·51 is the specific gravity of the carbonate with 8 atoms of water of crystallization, as given by Thomson. 1·423 is the specific gravity of the common crystallized carbonate with 10 atoms of water, as given by Haidinger. The specific gravities of the 36 solutions are all from my experiments. The discrepancies in the results of these experiments are very great. Carbonate of soda is a troublesome substance to examine, in consequence of the extreme facility with which it crystallizes. Finding it impossible to obtain concurrent results, I have quoted duplicate experiments to give an idea of the general range of the reactions that take place.

*Observations on the Table of Carbonate of Soda.*

The strongest solution of carbonate of soda prepared at 62° F. has the sp. gr. of 1·166, and a chemical strength of 185°. Its formula is nearly $NaO, CO^2 + 33H^2O$. A solution of sp. gr. 1·16657 deposited crystals while weighing at 62° F. The solution of sp. gr. 1·166, if cooled a little below 62° F., also deposits crystals. The exact point of saturation is difficult to hit. I made many trials with perfectly pure materials, and always weighed a quantity that filled a bottle of the capacity of 3000 grs. of water. I believe that the sp. gr. 1·166 is very near the truth. It differs considerably however from the usual quotations. Dr. Thomson states the specific gravity of a saturated solution at $58\frac{1}{4}$° F. to be 1·07516. This is no doubt a misprint for 1·17516. Dr. Henry quotes the specific gravity at the temperature of the atmosphere to be 1·26. This also seems to be a misprint for 1·16.

The greatest amount of condensation occurs in the solution of sp. gr. 1·166, coincident with the greatest chemical strength and greatest density, as is the case with solutions of all the fixed alkalies described in this memoir.

The measure of the test atom of anhydrous carbonate of soda is 38·66 septems, or a little above that of anhydrous sulphuric acid. The measure diminishes rapidly as the salt combines with water, and in a solution of 1° the atomic volume is reduced to −70·38 septems, showing a difference of 109 septems. The condensation produced by the combination of carbonate of soda with water *exceeds* that produced by the hydration of sulphuric acid. Thus, 1 test atom of each substance, combined with different proportions of water, effects the following condensations, expressed in septems:—

| Atoms of water. | 1 $NaO, CO^2$ condenses: | 1 $SO^3$ condenses: |
|---|---|---|
| 8 | 19 septems. | 15 septems. |
| 33 | 33 ... | 19 ... |
| 62 | 37 ... | 22 ... |
| 1038 | 55 ... | 37 ... |
| 6227 | 109 ... | 105 ... |

The fraction which +1 indicates the mean specific gravity of 100° of carbonate of soda is (1·4659+25·866=) ·056673.

There is a particular hydrate of carbonate of soda, the chemical degree of which is about 90, where the condensation is equal to the volume of the test atom of the anhydrous salt. If a solution be made at this stage of dilution, of course the substance will dissolve without altering the bulk of the water.

If, to the same quantity of salt, less water be taken, there will be an expansion of the volume of the water; but if more water be taken, there will be a visible condensation.

Messrs. Playfair and Joule place carbonate of soda among the substances that dissolve in water without changing the volume of the water, and they give an experiment to prove its possession of this property. (Mem. Chem. Soc. ii. 414.) But the experiment proves nothing beyond the fact mentioned in the last paragraph. It shows a property characteristic of a particular solution, but not a property manifested by the salt in all its solutions. Instead of being a general character it is only a speciality.

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I may perhaps be permitted to make here a passing remark on the theory of the aqueous solution of hydrates advanced by M. Gay-Lussac (*Ann. Chim. Phys.* t. lxx. p. 426):—

"As it is of interest to know whether a salt, susceptible of forming a hydrate, dissolves in water hydrated or anhydrous, I will cite a fact which appears to me sufficient to destroy the uncertainty. It is, that whenever an anhydrous salt, or any other body not having the property to form a hydrate, dissolves in water, there is always a production of cold, and that, on the contrary, whenever the salt can form a hydrate, there is a production of heat. When the hydrate is completed, previous to the solution in water, the case is the same as when the salt cannot form a hydrate. It is conceivable that it might sometimes happen, that the heat produced by hydration was less than the cold produced by the change of state, but I have not yet met with an exception."

The remark I wish to make on this passage is, that it is fallacious in ascribing the production of heat and cold (meaning thereby such as can be detected in the solutions by the thermometer), each to a single reaction. There is, according to my observations, always a double reaction, and it is for want of noticing the double reaction that the "exceptions" alluded to in the last sentence of the extract were never detected. It is due to this eminent philosopher to offer sufficient reasons for my objections to his opinions.

When a test atom of anhydrous carbonate of soda is dissolved in water much heat is disengaged. 38·66 septems of the salt combine with 160·7 septems of water, and produce 179·91 septems of hydrated carbonate of soda. Here there is a loss of volume equal to 19·45 septems, and this condensation is the source of the heat produced. But there is another reaction also to be taken into consideration: the 38·66 septems of dry salt, in combining with the 160·7 septems of

water, pass from the solid state to the liquid, and must absorb as much heat as is necessary to give them fluidity. The thermometric heat is the *difference* between the heat produced by condensation and the cold produced by change of state, and in the present example the heat predominates.

But when 179·91 septems of hydrated or crystallized carbonate of soda are dissolved in water, much cold is produced, though not in consequence of the occurrence of the single phænomenon of change of state from solidity to fluidity. It is true, that the liquefaction of 179·91 septems of crystals, and their dispersion through 23·29 atoms (=374·27 septems) of additional water, producing a liquid compound of the bulk of 540·54 septems, occasions the production of much cold, yet it must be observed that the crystallized hydrate, in forming this second hydrate, causes a condensation equal to 13·64 septems, which must unquestionably produce heat. But since in this experiment the mass of matter to be liquefied is almost five times greater than in the former example, while the amount of condensation is one-third less, the single thermometric result of the solution is a fall in temperature. Here then we have evidently that "exception" which M. Gay-Lussac was unable to find, that, namely, where "the heat produced by hydration is less than the cold produced by change of state." And this exception, so far from being a rarity, must occur in every case where the atomic measure of the substance to be liquefied is large, and its power of condensation but small. Without multiplying examples, I think I may safely assume, that in all cases of solution the thermometric heat or cold produced is not the effect of a single reaction, but is the *difference* between the heat disengaged by hydration and condensation, and the heat absorbed by liquefaction or expansion.

Upon this principle, it is easy to explain the heat produced when strong sulphuric acid and potash-ley are diluted with water, for as in these cases the substances are already liquid, the effect caused by condensation is predominant. We can also easily comprehend the cause of the great degree of cold produced by dissolving sal-ammoniac in water. I shall show, in a subsequent section, that 62·23 septems of anhydrous sal-ammoniac, on being dissolved in 256·70 septems of water, equal together to 318·93 septems, actually produce 326·80 septems of solution. Here the cold produced by the liquefaction of 62·23 septems of the solid salt is added to the cold produced by the expansion of 318·93 septems of solution to 326·80 septems, being an expansion of 7·87 septems—equal to one-eighth part of the bulk of the salt. And as in this

case no heat is disengaged, the whole effects of the cold are thermometric.

Gay-Lussac's idea, that the production of cold on solution is evidence that the substance dissolved cannot form a hydrate, or become any further hydrated, appears to me to be erroneous. How is it possible to account for the expansion which occurs on dissolving sal-ammoniac in a minimum of water, except by admitting the exercise of chemical action? or how account for the condensation it effects with a maximum of water, except by admitting the same agency? It seems to me, that *hydration* is evident in both cases, notwithstanding the production of cold. What other explanation also shall we give of the phænomena attending the solution of crystallized carbonate of soda? While in the very act of dissolving, under production of considerable cold, this salt simultaneously combines with an additional quantity of water, and causes a large amount of condensation. The heat disengaged by this condensation, being spent in liquefying the crystallized hydrate, is not sensible to the thermometer, which only detects the cold that remains in excess. But since the condensation certainly takes place and can be measured, it proves the thermometer to be a very fallible and incompetent guide in this field of research.

TABLE XV.—*Ammonia.*

$N^2 H^6 = 214{\cdot}47$ grs. Temperature 62° F.

| Authorities for the specific gravity. | Specific gravity of the solution. | Atoms of $N^2 H^6$ in 1000 septems. | Atoms of water to 1 $N^2 H^6$. | 1 $N^2 H^6$ | | Septems containing 1 atom of $N^2 H^6$. |
|---|---|---|---|---|---|---|
| | | | | Occupies: septems. | Expands: septems. | |
| F | ·76 | 24·805 | 0·0 | 40·31 | 0·0 | 40·314 |
| Dv | ·875 | 9·2816 | 3·96 | 44·11 | 3·80 | 107·74 |
| CD | ·8794 | 9·00 | 4·17 | 44·04 | 3·73 | 111·11 |
| CD | ·8962 | 8·00 | 5·06 | 43·62 | 3·31 | 125·00 |
| U | ·9 | 7·7843 | 5·29 | 43·48 | 3·17 | 128·46 |
| Dv | ·9 | 7·6374 | 5·43 | 43·73 | 3·42 | 130·93 |
| Dv | ·9054 | 7·4971 | 5·61 | 43·26 | 2·95 | 133·39 |
| CD | ·9116 | 7·00 | 6·20 | 43·27 | 2·96 | 142·86 |
| CU | ·9225 | 6·00 | 7·66 | 43·56 | 3·25 | 166·67 |
| CU | ·9347 | 5·00 | 9·73 | 43·70 | 3·39 | 200·00 |
| CU | ·9468 | 4·00 | 12·82 | 43·94 | 3·63 | 250·00 |
| CU | ·9603 | 3·00 | 18·01 | 43·87 | 3·56 | 333·33 |
| CU | ·97288 | 2·00 | 28·36 | 44·20 | 3·89 | 500·00 |
| CU | ·98666 | 1·00 | 59·50 | 43·98 | 3·67 | 1000·0 |
| CU | ·9936 | ·50 | 121·8 | 43·44 | 3·13 | 2000·0 |
| | | | Mean | 43·73 | 3·42 | |

AUTHORITIES.—Dv = Davy. F = Faraday. Ammonia gas condensed by the pressure of 6½ atmospheres at 50° Fahr. U = Ure. CD = Calculated after Davy's numbers. CU = Calculated after Ure's numbers.

*Observations on* Table XV.—*Ammonia.*

The measure of the test atom of ammonia, as existing in various solutions, varies from 44·20 septems to 43·26 septems. The mean of 14 examples is 43·73 septems. The differences among the determinations are all so small and so irregular as to be apparently mere errors of experiment. Ammonia therefore differs from the fixed alkalies, and from the acids, in having *a fixed atomic volume in solution.* If we compare this volume with the measure of the test atom of anhydrous liquid ammonia condensed by $6\frac{1}{2}$ atmospheres, we find an apparently constant expansion of about $3\frac{1}{2}$ septems; but of this expansion we have no corroborative evidence. It may occur, or it may not.

Reflecting upon the causes that could give to ammonia this peculiar property of a fixed atomic volume in solution, it occurred to me that there might be some relation between the corpuscular constitution of ammonia and that of water. The number of ultimate atoms in an equivalent of ammonia being 8, and those in an equivalent of water being 3, these numbers bear a near proportion to the apparent atomic measure of ammonia, 43·73, and the atomic measure of water, 16·07, the last of these two numbers being very nearly three-eighths of the preceding number. I thought it possible that solutions of ammonia might consist of compounds in which water and ammonia were united in the proportions indicated by those numbers. I tried to construct a table of solutions of ammonia on that principle, using the atomic numbers of Berzelius both for water and ammonia, but I did not succeed by this means in obtaining consistent results, and I considered the hypothesis to be untenable. Yet, previous to abandoning it, I thought it proper to try whether better results would ensue if the same principle was applied to the atomic numbers for water and ammonia that have been proposed by Thomson and Dumas. It gratified me to find that this threw a new light on the difficulty, and enabled me to calculate the following Table:—

## TABLE XVI.—*Ammonia.*

$N^2H^6 = 212{\cdot}5$ grs. Temperature 62° F.

| Specific gravity of the solution. | Atoms of $N^2H^6$ in 1000 septems. | Atoms of $H^2O$ to 1 atom $N^2H^6$. | Ratio of $N^2H^6$ | | 1000 septems of solution contain | | Septems containing 1 atom of $N^2H^6$. |
|---|---|---|---|---|---|---|---|
| | | | By weight. | By volume. | Grains of $N^2H^6$. | Grains of $H^2O$. | |
| ·708333 | 23·33 | 0·0 | 1·00 | 1·00 | 4958·3 | 0000 | 42·857 |
| ·787878 | 16·97 | 1· | ·65385 | ·727273 | 3606·1 | 1909 | 58·929 |
| ·833333 | 13·33 | 2· | ·48571 | ·571429 | 2833·3 | 3000 | 75·000 |
| ·862747 | 10·98 | 3· | ·38636 | ·470588 | 2333·3 | 3706 | 91·071 |
| ·875000 | 10·00 | 3·556 | ·34694 | ·428571 | 2125·0 | 4000 | 100·00 |
| ·883333 | 9·333 | 4· | ·32075 | ·40 | 1983·3 | 4200 | 107·14 |
| ·887500 | 9·00 | 4·247 | ·30785 | ·385714 | 1912·5 | 4300 | 111·11 |
| ·900000 | 8·00 | 5·111 | ·26984 | ·342857 | 1700· | 4600 | 125·00 |
| ·912500 | 7·00 | 6·222 | ·23288 | ·30 | 1487·5 | 4900 | 142·86 |
| ·925000 | 6·00 | 7·704 | ·19691 | ·257143 | 1275· | 5200 | 166·67 |
| ·937500 | 5·00 | 9·778 | ·16195 | ·214286 | 1062·5 | 5500 | 200·00 |
| ·950000 | 4·00 | 12·89 | ·12782 | ·171429 | 850· | 5800 | 250·00 |
| ·962500 | 3·00 | 18·07 | ·09462 | ·128571 | 637·5 | 6100 | 333·33 |
| ·975000 | 2·00 | 28·44 | ·062271 | ·085714 | 425· | 6400 | 500·00 |
| ·987500 | 1·00 | 59·55 | ·030741 | ·042857 | 212·5 | 6700 | 1000·0 |
| ·988750 | ·90 | 66·47 | ·027632 | ·038571 | 191·25 | 6730 | 1111·1 |
| ·990000 | ·80 | 75·11 | ·024531 | ·034286 | 170· | 6760 | 1250·0 |
| ·991250 | ·70 | 86·22 | ·021438 | ·03 | 148·75 | 6790 | 1428·6 |
| ·992500 | ·60 | 101·4 | ·018352 | ·025714 | 127·5 | 6820 | 1666·7 |
| ·993750 | ·50 | 121·8 | ·015274 | ·021429 | 106·25 | 6850 | 2000·0 |
| ·995000 | ·40 | 152·9 | ·012204 | ·017143 | 85· | 6880 | 2500·0 |
| ·996250 | ·30 | 204·7 | ·009141 | ·012857 | 63·75 | 6910 | 3333·3 |
| ·997500 | ·20 | 308·4 | ·006101 | ·008571 | 42·5 | 6940 | 5000·0 |
| ·998750 | ·10 | 619·5 | ·003040 | ·004286 | 21·25 | 6970 | 10000· |
| ·998875 | ·09 | 688·7 | ·002735 | ·003857 | 19·125 | 6973 | 11111· |
| ·999000 | ·08 | 775·1 | ·002431 | ·003429 | 17· | 6976 | 12500· |
| ·999125 | ·07 | 886·2 | ·002127 | ·003 | 14·875 | 6979 | 14286· |
| ·999250 | ·06 | 1034· | ·001823 | ·002571 | 12·75 | 6982 | 16667· |
| ·999375 | ·05 | 1242· | ·001519 | ·002143 | 10·625 | 6985 | 20000· |
| ·999500 | ·04 | 1553· | ·001215 | ·001714 | 8·5 | 6988 | 25000· |
| ·999625 | ·03 | 2071· | ·000911 | ·001286 | 6·375 | 6991 | 33333· |
| ·999750 | ·02 | 3108· | ·000607 | ·000857 | 4·25 | 6994 | 50000· |
| ·999875 | ·01 | 6220· | ·000304 | ·000429 | 2·125 | 6997 | 100000· |
| 1·00000 | 62·22 | Water, test atom = 112·5 grs. | | | | 7000 | 16·0714 |

### *Observations on* Table XVI.—*Ammonia.*

The table of ammonia is calculated on the following principles:—The atom of water is assumed to weigh 112·5 grs., and to measure 16·071429 septems. The atom of ammonia is assumed to weigh 212·5 grs., and to measure 42·857143 septems. The relation of these measures is as follows:—

$$16{\cdot}071429 \times \frac{8}{3} = 42{\cdot}857143.$$

The ammonia and water are assumed to combine together in all cases without any alteration of measure. The composition

of solution of 100°, or 1 test atom of ammonia per decigallon, is calculated thus :—

| | | |
|---|---|---|
| 42·857143 | septems | = bulk of 1 test-atom of $N^2 H^6$. |
| 957·142857 | ... | = water required to complete 1000 sept. |
| 6700· | grs. | = weight of that measure of water. |
| 212·5 | ... | = weight of 1 test atom of $N^2 H^6$. |
| 6912·5 | ... | = weight of 1000 septems of solution. |

Corresponding specific gravity $\frac{6912{\cdot}5}{7000} = {\cdot}987500$.

The ratio of $N^2 H^6$ by weight is $\frac{212{\cdot}5}{6912{\cdot}5} = {\cdot}030741$.

We have thus the weight and the volume of the water, the weight and the volume of the ammonia, and the weight and volume of the resulting solution : in short, all the details necessary to give a complete knowledge of the physical constitution of the compound.

The other solutions were all calculated in the same way.

The weight of 1°, the hundredth part of a test atom, of ammonia, is 2·125 grs. ; its volume at 62° F. is precisely equal to that of 3 grs. of water. Every degree of ammonia, added to an aqueous solution, displaces 3 grs. of water, reduces the weight of a decigallon of solution to the extent of $3 - 2{\cdot}125 = {\cdot}875$ grs., and lessens the specific gravity by ·000125. From this principle proceed two important practical rules :—

I. *Given, the specific gravity of a solution of ammonia, to find its chemical strength.*

Deduct the specific gravity from 1·000000, and divide the remainder by ·000125. The product is the chemical strength expressed in degrees.

II. *Given, the chemical strength of a solution of ammonia, to find its specific gravity.*

Express the chemical strength in degrees ; multiply it by ·000125, and deduct the product from 1·000000. The remainder is the required specific gravity.

The four solutions at the head of the list, separated from the others by a horizontal line, are such as do not exist at the temperature of 62° F. The first line is anhydrous ammonia, assumed to retain its usual volume at 62° F. though free from water. The second line is the supposititious oxide of ammonia = $N^2H^8O$. The third line is the hydrate of that assumed oxide = $N^2H^8O + H^2O$, corresponding to caustic potash. The fourth line represents the last compound with an additional atom of water = $N^2H^8O + 2H^2O$. The chemical strength of this third hydrate is 1098°. Now I have procured

at 42° F. a solution of the chemical strength of 1120°, so that this third hydrate is easily obtainable at a temperature between 42° F. and 62° F.; and the preparation of even the second hydrate ($N^2H^8O + H^2O$) is perhaps possible at a lower temperature. At 62° F. however, the solution of 1000° was the strongest I could prepare.

An examination of this table leads naturally to the questions, how far is it to be relied on? how nearly does it agree with the results of experiment? I cannot answer these questions better than by giving an abstract of a series of experiments made expressly to test the validity of the hypothesis. These experiments are embraced in Table XVII.

## Table XVII.—*Ammonia.*

Experiments on the Specific Gravity of Solutions of Ammonia, of known chemical strength. Temperature 62° F.

| Chemical strength in atoms. | Specific gravity: By theory. | Specific gravity: By trial. | Difference. | Chemical strength in atoms. | Specific gravity: By theory. | Specific gravity: By trial. | Difference. |
|---|---|---|---|---|---|---|---|
| 10·20 | ·872500 | ·875943 | − 27½° | ·90 | ·988750 | ·988672 | + ½° |
| 10·00 | ·875000 | ·875175 | − 1½ | ·90 | ·988750 | ·988657 | + ¾ |
| 9·975 | ·875313 | ·875175 | + 1 | ·80 | ·990000 | ·990057 | − ½ |
| 9·95 | ·875625 | ·880629 | − 40 | ·80 | ·990000 | ·990086 | − ⅝ |
| 9·80 | ·877500 | ·880629 | − 25 | ·70 | ·991250 | ·991086 | + 1¼ |
| 9·00 | ·887500 | ·894229 | − 54 | ·60 | ·992500 | ·992629 | − 1 |
| 9·00 | ·887500 | ·887943 | − 3½ | ·60 | ·992500 | ·992857 | − 3 |
| 8·10 | ·898750 | ·898572 | + 1½ | ·50 | ·993750 | ·993714 | + ⅓ |
| 8·00 | ·900000 | ·900286 | − 2¼ | ·40 | ·995000 | ·995429 | − 3½ |
| 8·00 | ·900000 | ·901714 | − 13¾ | ·40 | ·995000 | ·995315 | − 2½ |
| 7·90 | ·901250 | ·901567 | − 2½ | ·40 | ·995000 | ·995200 | − 1½ |
| 7·63 | ·904625 | ·905143 | − 4 | ·30 | ·996250 | ·996143 | + ¾ |
| 7·55 | ·905625 | ·906500 | − 7 | ·30 | ·996250 | ·996171 | + ½ |
| 7·00 | ·912500 | ·912829 | − 2½ | ·20 | ·997500 | ·997886 | − 3 |
| 6·85 | ·914375 | ·913857 | + 4 | ·20 | ·997500 | ·997800 | − 2½ |
| 6·80 | ·915000 | ·915333 | − 2½ | ·10 | ·998750 | ·998714 | + ¼ |
| 6·00 | ·925000 | ·925086 | − ¾ | ·10 | ·998750 | ·998771 | − ¼ |
| 5·00 | ·937500 | ·937514 | − } 0 | ·10 | ·998750 | ·998857 | − ¾ |
| 5·00 | ·937500 | ·937486 | + } | ·09 | ·998875 | ·998971 | − ¾ |
| 4·05 | ·949385 | ·949267 | + 1 | ·08 | ·999000 | ·999029 | − ¼ |
| 4·00 | ·950000 | ·949686 | + 2¼ | ·07 | ·999125 | ·999114 | + |
| 4·00 | ·950000 | ·949600 | + 3¼ | ·06 | ·999250 | ·999257 | − |
| 3·00 | ·962500 | ·962143 | + 3 | ·05 | ·999375 | ·999400 | − ¼ |
| 2·00 | ·975000 | ·974429 | + 4½ | ·04 | ·999500 | ·999514 | − } 0 |
| 2·00 | ·975000 | ·974629 | + 3 | ·04 | ·999500 | ·999486 | + } |
| 1·00 | ·987500 | ·987229 | + 2 | ·03 | ·999625 | ·999600 | + |
| 1·00 | ·987500 | ·987257 | + 2 | ·02 | ·999750 | ·999743 | + |
| 1·00 | ·987500 | ·987514 | | ·01 | ·999875 | ·999857 | + } 0 |
| 1·00 | ·987500 | ·987543 | − ¼ | ·01 | ·999875 | ·999886 | − } |

The chemical strength of the solutions that were examined was determined by neutralization with pure muriatic acid, the strength of which was ascertained by means of carbonate of soda and nitrate of silver. The specific gravities were determined by weighing the liquors in stoppered glass bottles at the temperature of 62° F. I have placed side by side the theoretical densities and those determined by experiment, and I have added a column of differences, to show in what cases and to what extent the experimental specific gravity indicated a greater or lesser chemical strength than the theoretical specific gravity. If in any of these solutions there had occurred either condensation or expansion, it would be shown in this column, where however are also shown all the errors of experiment. These errors are very great in the experiments on concentrated solutions, and they are unavoidable. A solution of ammonia of 1000° *effervesces* when a warm finger is applied to the bottle containing it. In general the specific gravity determined by experiment is too high, for this reason, that when a concentrated solution is prepared and adjusted to the required temperature it takes but little time to transfer a graduated pipetteful of it into a stoppered bottle containing water to dilute it for chemical examination; whereas, the transferring of a quantity of the undiluted solution to a weighing bottle, the adjustment of the measure, and the accurate weighing, occupy much time, occasion considerable exposure to the air, and permit a large escape of gas. Below 800° this difficulty is much less, and the differences are probably errors of experiment. There is however one part of the Table in which the differences between the computed and experimental specific gravities seem to indicate the occurrence of expansion. This is between 500° and 100°, and it is among solutions of this strength that Dr. Ure found similar differences to exist between experimental and computed densities; from which differences he drew the conclusion, that solutions of ammonia expand when they are diluted. I subjoin his experiments:—

| Computed or mean specific gravity. | Specific gravity by experiment. | Computed or mean specific gravity. | Specific gravity by experiment. |
|---|---|---|---|
| ·90452 | ·9045 | ·94737 | ·9455 |
| ·90909 | ·909 | ·95744 | ·9564 |
| ·91838 | ·9177 | ·96774 | ·9662 |
| ·9278 | ·9275 | ·97826 | ·9768 |
| ·9375 | ·9363 | ·989 | ·9887 |

—*Tilloch's Philosophical Magazine*, vol. lvii.

The approximate coincidence of my experiments with Dr. Ure's will perhaps be held to prove the correctness of his opinion; and I must admit that there is some appearance of the occurrence of a slight expansion at about 300°. Yet this apparent expansion is so small, and the figures that indicate it are so likely to be merely the expression of errors of experiment, that I consider the expansion, though possible, not by any means proved. The evidence tending to prove that ammonia has a fixed atomic volume in solution, seems to me greatly to preponderate over that which indicates expansion. My doubts respecting the occurrence of expansion were further strengthened by the results of the following experiment.

Into a long narrow graduated bottle I put 500 septems of strong commercial ammonia, the degree of which was 810°. Its specific gravity was 0·898572 by trial. By means of a bottle so graduated as to *deliver* 500 septems of water, I added that quantity to the ammonia. The bottle was stopped, wrapped in a thick towel, and briskly shaken for about a minute. Each liquor previous to the mixture was brought to the temperature of 51° F. Immediately after the shaking, the temperature was found to be 54° F. Here was a rise of 3°, indicating, not expansion, but condensation. When the liquor had returned to 51° F. its volume was examined. There certainly was no expansion. I think there was a slight condensation, but it was scarcely measurable. The chemical strength of the diluted liquor was found to be 406°. This indicated condensation. Its specific gravity was ·950600, and since $(\cdot 898572 + 1) \div 2 = \cdot 949286$, this also indicated condensation.

The results which in this experiment indicate condensation are, I believe, as remote from the truth as those which in other experiments seemed to indicate expansion. One of these results is remarkable, namely, the rise in temperature which apparently results from the combination of the two liquids. If water and liquid ammonia combine without change of volume, there should be no change of temperature. To what cause then shall we attribute the rise of 3° F.? To agitation alone? That, I think, is sufficient to account for it.

I cleaned the bottle from ammonia, put into it a decigallon of distilled water, and shook it for one minute. The temperature rose from 49° to 49½° F. Half a gallon of water shaken in a larger bottle rose from 43½° to 44¼°. 3000 septems rose from 49¾° to 50¼°. A solution of pure carbonate of potash rose from 50½° to 51½°. A solution of pearlash

from $50\frac{1}{2}°$ to $51\frac{1}{2}°$. A solution of bicarbonate of potash from $50\frac{1}{2}°$ to $51\frac{3}{4}°$. Oil of vitriol from $51\frac{1}{2}°$ to $52\frac{1}{4}°$.

These experiments show how difficult it is to determine the amount of heat that is disengaged when liquors are mixed, since the agitation necessary to effect the mixture can of itself produce part of the rise of temperature which is attributed wholly to the chemical action of the substances mixed together.

I shall conclude this notice of ammonia by referring to a fact of considerable importance which is disclosed in Table XVI. This is, that it is impossible to state accurately the specific gravity of solutions of ammonia with less than six places of decimals, since the effect of every chemical degree on the specific gravity is ·000125. Thus while a solution of 800° is accurately expressed by ·9 or ·900000, a solution of 799° requires ·900125, and a solution of 801° requires ·899875. This peculiarity ought to be attended to in future researches on aqueous solutions.

This observation leads me to make another which may be interesting to practical men, who are accustomed to estimate the value of ammonia and similar liquors after the indications afforded by hydrometers that have scales with large divisions —Twaddell's, Baumé's, and the like. Now 40 chemical degrees of ammonia, or $\frac{2}{5}$ of a test atom, affect the density of the liquor only so much as answers to 1 degree of the scale of Twaddell's hydrometer. Such an instrument therefore, if perfect in construction, and used with unerring skill, is unfit to tell the strength of solutions of slight density, such as those of ammonia and acetic acid: methods of chemical testing are greatly preferable.

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Since the preceding section on ammonia was written, I have seen an abstract of Dr. Faraday's recent researches concerning condensed gases. In that it appears that his present estimate of the specific gravity of condensed liquid ammonia at 60° F. is 0·731. His former estimate was 0·76. The specific gravity which theoretical considerations led me to adopt for anhydrous liquid ammonia at 62° F. is 0·708333. This differs from Dr. Faraday's new experimental determination by only 0·022667. The number of test atoms of ammonia contained in a decigallon is, according to Dr. Faraday's specific gravity, 24·08, according to mine 23·33. The difference is only $\frac{3}{4}$ of a test atom per decigallon. The atomic measure

of a test atom of ammonia, according to Dr. Faraday's specific gravity, is 41·5282, according to mine 42·8571 septems. The difference is 1·3289 septems. Hence my assumptions are almost confirmed by Dr. Faraday's experiments.

## TABLE XVIII.—*Sal-Ammoniac.*

$H^2Cl^2 + N^2H^6 = 667{\cdot}63$ grs. Temperature 62° F.

$[H^2Cl^2 = 455{\cdot}13 + N^2H^6 = 212{\cdot}5.]$

| Authorities for the specific gravity. | Specific gravity of the solution. | Atoms of $H^2Cl^2N^2H^6$ in 1000 septems. | Atoms of water to 1 $H^2Cl^2 + N^2H^6$. | 1 $H^2Cl^2$, $N^2H^6$ | | Septems of solution containing 1 $H^2Cl^2$, $N^2$ $H^6$. |
|---|---|---|---|---|---|---|
| | | | | Occupies: septems. | Condenses: septems. | |
| Kp | 1·5 | 15·727 | 0·0 | 63·58 | 0·0 | 63·584 |
| Hk | 1·525 | 15·992 | 0·0 | 62·53 | 0·0 | 62·531 |
| Ms | 1·528 | 16·021 | 0·0 | 62·42 | 0·0 | 62·419 |
| PJ | 1·578 | 16·545 | 0·0 | 60·44 | 0·0 | 60·441 |
| Mean | 1·53275 | 16·071 | 0·0 | 62·23 | 0·0 | 62·225 |
| G | 1·077333 | 3·06 | 15·97 | 70·10 | −7·87 | 326·80 |
| G | 1·075829 | 3·00 | 16·38 | 70·10 | −7·87 | 333·33 |
| G | 1·054114 | 2·00 | 26·86 | 68·32 | −6·09 | 500·00 |
| Hk | 1·032300 | 1·2076 | 47·26 | 68·63 | −6·40 | 828·11 |
| G | 1·028658 | 1·00 | 58·07 | 66·72 | −4·49 | 1000·0 |
| G | 1·028686 | 1·00 | 58·08 | 66·69 | −4·46 | 1000·0 |
| G | 1·026086 | ·90 | 65·01 | 66·39 | −4·16 | 1111·1 |
| G | 1·023029 | ·80 | 73·64 | 66·59 | −4·36 | 1250·0 |
| G | 1·020200 | ·70 | 84·76 | 66·52 | −4·29 | 1428·6 |
| G | 1·017571 | ·60 | 99·60 | 66·09 | −3·86 | 1666·7 |
| G | 1·014743 | ·50 | 120·4 | 65·89 | −3·66 | 2000·0 |
| G | 1·011800 | ·40 | 151·5 | 65·88 | −3·65 | 2500·0 |
| G | 1·009143 | ·30 | 203·4 | 64·90 | −2·67 | 3333·3 |
| PJ | 1·008800 | ·27881 | 219·2 | 63·81 | −1·58 | 3586·6 |
| G | 1·006257 | ·20 | 307·1 | 64·09 | −1·86 | 5000·0 |
| G | 1·004657 | ·15 | 410·8 | 64·33 | −2·10 | 6666·7 |
| G | 1·004000 | ·125 | 493·9 | 63·38 | −1·15 | 8000·0 |
| G | 1·003514 | ·10 | 618·5 | 60·23 | 2·00 | 10000·0 |
| G | 1·003486 | ·10 | 618·5 | 60·52 | 1·71 | 10000·0 |
| G | 1·003143 | ·09 | 687·6 | 60·46 | 1·77 | 11111· |
| G | 1·002886 | ·08 | 774·1 | 59·30 | 2·93 | 12500· |
| G | 1·002657 | ·07 | 885·4 | 57·42 | 4·81 | 14286· |
| G | 1·002371 | ·06 | 1034· | 55·85 | 6·38 | 16667· |
| G | 1·001971 | ·05 | 1241· | 55·95 | 6·28 | 20000· |
| G | 1·001543 | ·04 | 1552· | 56·80 | 5·43 | 25000· |
| G | 1·001714 | ·04 | 1552· | 52·52 | 9·71 | 25000· |
| G | 1·001114 | ·03 | 2071· | 58·23 | 4·00 | 33333· |
| G | 1·000800 | ·02 | 3108· | 55·37 | 6·86 | 50000· |
| G | 1·000457 | ·01 | 6219· | 49·66 | 12·57 | 100000· |
| 1 | 2 | 3 | 4. | 5 | 6 | 7 |

AUTHORITIES.—Kp = Kopp. Hk = Holker. Ms = Mohs. PJ = Playfair and Joule. All these relate to the specific gravity of anhydrous sal-ammoniac. I have adopted the mean as the true number. The solutions are all described from my experiments, except the two marked Holker and Playfair and Joule.

*Observations on the Table of Sal-Ammoniac.*

I have adopted for the weight of the test atom of sal-ammoniac Berzelius's number for muriatic acid, added to Thomson's number for ammonia; my object being to afford a means of comparing solutions of sal-ammoniac at given strengths with those of muriatic acid and ammonia at the same strengths, quoted in other sections of this memoir.

The strongest solution of sal-ammoniac at 62° F. has the specific gravity of 1·077333 and the chemical strength of 306°. Its formula is probably $H^2Cl^2$, $N^2H^6 + 16H^2O$. This solution gives a considerable deposit of crystals when cooled to 59° F. The measure of the test atom of the anhydrous salt is 62·23 septems. When existing in the solution of 306° its measure is increased to 70·10 septems. When in a solution of 1° its measure is diminished to about 50 septems. At an intermediate point, somewhere about 12°, the measure of the atom in solution is the same as that of the anhydrous atom. Hence sal-ammoniac has no fixed volume in solution, but possesses the property of causing *expansion* in strong solutions and *condensation* in weak solutions.

The atomic measure of sal-ammoniac is never the same as the joint measure of muriatic acid and ammonia. The differences at different stages of dilution are as follow:—

| Chemical strength of the solutions. | Measure of $H^2Cl^2$ added to that of $N^2H^6$. | Measure of Sal-ammoniac. | Difference or condensation. |
|---|---|---|---|
| ° | Septems. | Septems. | Septems. |
| 300 | 79 | 70 | 9 |
| 200 | 78 | 68 | 10 |
| 100 | 77 | 67 | 10 |
| 50 | 76 | 66 | 10 |
| 10 | 76 | 60 | 16 |
| 5 | 76 | 56 | 20 |
| 1 | 78 | 50 | 28 |

Messrs. Playfair and Joule seem to be of opinion that when we know the atomic measure of a compound, A B, and that of one of its components, A, then, by taking the difference, we can find the true measure of the other component, B. It is clear, however, that this is not the case with sal-ammoniac; for this salt, when at its state of greatest expansion, has a smaller atomic measure than ammonia *plus* muriatic acid when the latter is at its point of greatest condensation. Hence any attempt to determine the atomic measure of ammonia from a knowledge of the atomic measures of muriatic acid and of sal-ammoniac must lead only to bewilderment.

The fraction which +1 indicates the mean specific gravity of 100° of sal-ammoniac is (·53257÷16·071=) ·033150.

It follows from what has been stated, that the real specific gravity of solutions of sal-ammoniac must be *less* than the mean specific gravity when the chemical strength is above 12°, and *greater* than the mean specific gravity when the chemical strength is below 12°.

*Examples*:—

| | 100° | | 10° |
|---|---|---|---|
| Mean sp. gr. . | 1·033150 | Mean sp. gr. . | 1·003315 |
| Deduct . . . | 0·004490 | Add . . . . | 0·000200 |
| Real sp. gr. . | 1·028660 | Real sp. gr. . | 1·003515 |

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The following experiments were made to determine the correctness of the number assumed for the atomic weight of sal-ammoniac.

1. A solution of 66·763 grs. of sal-ammoniac mixed with a solution of 212·864 grs. of crystallized nitrate of silver, required half a septem of solution of nitrate of silver of 10° to complete the precipitation.

2. A solution of 66·96 grs. of sal-ammoniac (Berzelius's number) mixed with a solution of 212·864 grs. of nitrate of silver, required 3 septems of solution of nitrate of silver of 10° to complete the precipitation.

These experiments tend to prove that, taking for granted the accuracy of Berzelius's number for nitrate of silver, his number for sal-ammoniac is too high. But if, as the above experiments seem to show, 667·63 is the correct number for sal-ammoniac, then 212·5 is the correct number for ammonia, as I have assumed it to be in Table XVI.

## Table XIX.—*Sugar.*

$C^{12} H^{22} O^{11}$ = 2154 grs. Temperature 62° F.

| Authorities for the specific gravity. | Specific gravity of the solutions. | Atoms of $C^{12} H^{22} O^{11}$ in 1000 septems. | Atoms of water to 1 $C^{12} H^{22} O^{11}$. | 1 $C^{12} H^{22} O^{11}$ | | Septems of solution containing 1 $C^{12} H^{22} O^{11}$. |
|---|---|---|---|---|---|---|
| | | | | Occupies: septems. | Condenses: septems. | |
| F | 1·6 | 5·1996 | 0·0 | 192·32 | 0·0 | 192·32 |
| PJ | 1·596 | 5·1866 | 0·0 | 192·80 | 0·0 | 192·80 |
| PJ | 1·3866 | 3·3796 | 6·383 | 193·32 | −1·00 | 295·89 |
| U | 1·326 | 2·8728 | 9·574 | 194·24 | −1·92 | 348·10 |
| PJ | 1·2329 | 2·0034 | 19·15 | 191·46 | ·86 | 499·16 |
| U | 1·231 | 2·0002 | 19·15 | 192·23 | ·09 | 499·94 |
| U | 1·1777 | 1·5309 | 28·72 | 191·64 | ·68 | 653·21 |
| U | 1·144 | 1·2392 | 38·30 | 191·51 | ·81 | 806·95 |
| U | 1·134 | 1·1516 | 42·13 | 191·35 | ·97 | 868·33 |
| U | 1·125 | 1·0753 | 45·95 | 191·47 | ·85 | 929·97 |
| U | 1·111 | ·95014 | 53·62 | 190·89 | 1·43 | 1052·5 |
| U | 1·1045 | ·89734 | 57·44 | 191·26 | 1·06 | 1114·4 |
| U | 1·0905 | ·77044 | 68·93 | 190·25 | 2·07 | 1298·0 |
| U | 1·082 | ·70325 | 76·60 | 191·11 | 1·21 | 1422·0 |
| U | 1·0685 | ·57871 | 95·75 | 189·34 | 2·98 | 1728·0 |
| U | 1·05 | ·42653 | 134·0 | 190·49 | 1·83 | 2344·5 |
| U | 1·0395 | ·33781 | 172·3 | 190·79 | 1·53 | 2960·2 |
| PJ | 1·0367 | ·30627 | 191·5 | 187·89 | 4·43 | 3265·1 |
| PJ | 1·00566 | ·04405 | 1401· | 179·22 | 13·10 | 22702· |
| PJ | 1·00352 | ·02696 | 2298· | 177·11 | 15·21 | 37103· |
| PJ | 1·0035 | ·02658 | 2330· | 176·02 | 16·30 | 37627· |
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |

Authorities.—F = Fahrenheit. PJ = Playfair and Joule, Mem. Chem. Soc., ii. 407 and 416. U = Ure, Dict. of Arts, article Sugar. The first two lines represent anhydrous sugar. The others are all solutions.

### *Observations on the Table of Sugar.*

The experiments of Messrs. Playfair and Joule corroborate those of Dr. Ure, though made in a different manner and for a different purpose. According to the experiments of both parties, when sugar is dissolved in water so as to form a strong solution, there is an *expansion* of volume. The volume of the solution exceeds the volume of the two ingredients. When more water is added *condensation* ensues, and is carried by continued dilution to such an extent, that, according to the experiments of Messrs. Playfair and Joule, in a solution of sp. gr. 1·0035, the condensation effected by 1 test atom of sugar is equal to 16·30 septems, or more than the measure of an atom of water.

The volume of 1 test atom of water being 16·07 septems, that of 11 test atoms is 176·77 septems, and that of 12 test atoms is 192·84 septems. The atomic measure of anhydrous

sugar is 192·32 septems, or equal to that of 12 test atoms of water. Its measure in solution varies from 194·24 septems to 176·02 septems. Hence, in one very dilute solution of sugar, its atomic volume, as stated by Dalton and by Messrs. Playfair and Joule (Mem. Chem. Soc., vol. ii. page 418), is equal to that of 11 atoms of water, but, in highly concentrated solutions, its atomic volume, according to the experiments both of Dr. Ure and of Messrs. Playfair and Joule, is equal to more than that of 12 atoms of water. Sugar, therefore, has no fixed atomic volume in solution. It does not uniformly add to the bulk of the water of solution, a volume equivalent to its own oxygen and hydrogen estimated as water. Nor does its carbon cease to occupy space in solution. In short, Dalton's experiments on this subject are incorrect, his hypothesis is untenable, and the application of this method of analysis to organic bodies is impossible. Witness, acetic acid.

TABLE XX.—*Sulphate of Magnesia.*

$MgO, SO^3 = 759{\cdot}518$ grs. Temperature 62° F.
$MgO, SO^3 + 7H^2O = 1546{\cdot}878$ grs.

| Authorities for the specific gravity. | Specific gravity of the solution. | Atoms of the salt in 1000 septems. | $MgO, SO^3 + 7H^2O$ occupies: septems. | Anhydrous $MgO, SO^3$ occupies: septems. | $MgO, SO^3$ condenses: septems. |
|---|---|---|---|---|---|
| Kn | 2·6066 | 24·023 | ..... | 41·63 | ..... |
| Kp | 1·674 | 7·5753 | 132·01 | 19·53 | 22·10 |
| Hk | 1·665 | 7·5345 | 132·72 | 20·24 | 21·39 |
| D | 1·30 | 3·5944 | ..... | 25·04 | 16·59 |
| D | 1·05 | ·55298 | ..... | 18·08 | 23·55 |
| ..... | ..... | ..... | ..... | ..... | ..... |
| A | 1·270 | 2·7218 | 121·78 | 9·30 | 32·33 |
| A | 1·150 | 1·4868 | 120·10 | 7·62 | 34·01 |
| Hk | 1·1284 | 1·2734 | 120·15 | 7·67 | 33·96 |
| A | 1·128 | 1·2373 | 117·53 | 5·05 | 36·58 |
| A | 1·107 | 1·0334 | 117·44 | 4·96 | 36·67 |
| A | 1·055 | ·51137 | 113·41 | 0·93 | 40·70 |
| A | 1·010 | ·08958 | 109·35 | − 3·13 | 44·76 |
| A | 1·006 | ·04507 | 87·84 | −24·64 | 66·27 |

AUTHORITIES.—A = Anthon (temperature of solutions 59° F.). D = Dalton. Hk = Holker. Kn = Karsten. Kp = Kopp.

*Observations on the Table of Sulphate of Magnesia.*

Sulphate of magnesia is a substance regarding whose peculiar properties Messrs. Playfair and Joule are in strict accordance with Dr. Dalton. They find, with him, that when it dissolves in water it occupies no space in solution (Mem. Chem. Soc., vol. ii. p. 418).

As I also find that this fact is capable of experimental proof, it is necessary to inquire how it happens that the fact is true while the hypothesis that has been founded upon it is fallacious. The matter is not mysterious.

One test atom of anhydrous sulphate of magnesia measures, in round numbers, 42 septems. When this combines with 7 atoms of water to form the crystallized salt, it condenses 22 septems, and retains 20 septems as its measure in combination. These facts result from the experiments of Karsten, Kopp, and Holker, cited in the Table.

In the year 1810 Dalton published some experiments on solutions of this salt, of which, as they are inaccurate, I have only quoted two, the first and the last. According to these, when the solution has a specific gravity of 1·30, the measure of the test atom of anhydrous salt is 25 septems; but when the specific gravity is 1·05, the measure of the test atom is only 18 septems. These experiments, if correct, would prove three interesting points:—1. That the salt expands 5 septems per test atom on being liquefied by solution. 2. That it possesses a considerable volume in solution. 3. That the volume in solution is variable. These results are in direct opposition to Dalton's recent speculations.

Anthon's experiments show that the test atom of anhydrous sulphate of magnesia occupies about 9 septems in a solution of sp. gr. 1·27; that it gradually diminishes in bulk with the progress of the dilution, becomes nothing in a solution of sp. gr. 1·05, and in still weaker solutions effects great condensation, which in the last solution of sp. gr. 1·006, amounts to no less than 66 septems, or $\frac{3}{2}$ of the volume of the anhydrous salt. Anthon's experiments were made with the crystallized salt; but since the measure of 7 atoms of water is 112·48 septems, the reduction to the anhydrous salt is easy and obvious. Anthon's Table is contained in Gmelin's *Handbuch der Chemie, vierte Auflage*, t. ii. p. 235*.

Holker's experiment corroborates the experiments of Anthon, as far as a single experiment can serve as evidence in a case of this nature.

These researches show that anhydrous sulphate of magnesia, contrary to Dalton's late assumption, *does* occupy space when in strong solutions; that in weak solutions it occasions a condensation greater than its own volume; and that, at a certain intermediate point, it effects no condensation and oc-

* It is due to Professor Gmelin to state, that I am indebted for many facts and authorities quoted in this memoir to the new edition of his *Handbuch der Chemie*, the most comprehensive, accurate, and convenient systematic work on Chemistry that ever issued from the press.

cupies no space in solution. The solution which corresponds to this turning-point has a chemical strength of about 50°, and a specific gravity of nearly 1·05. Were a solution of sulphate of magnesia to be carefully made with proportions of salt and water corresponding to this stage of dilution, the result would appear to corroborate the late experiments of Dalton and of Messrs. Playfair and Joule, and thus a very accurate experiment might be made to support a very fallacious theory.

This last remark applies equally to many other substances whose examination is described in this memoir, and it shows the danger of drawing a sweeping conclusion from the results of any single experiment, however accurately performed. Thus, in the case of sulphuric acid, if we were to adopt the rash principle of deciding upon the atomic measure from the results of a single experiment, we could prove the atomic measure of that acid to be 2 volumes, or 1 volume, or nothing, or less than nothing; in short, anything we pleased between *plus* 34 septems and *minus* 68 septems; for we could pick out an accurate experiment to yield any numerical product that best suited a given purpose within those limits.

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## CLXIX. *Researches on Atomic Volume and Specific Gravity.* *By* James P. Joule, *Esq.* *and* Dr. Lyon Playfair.

### Series III.—*On the Maximum Density of Water.*

In all researches on specific gravity the selection of a proper standard of comparison is a matter of great importance. For obvious reasons water has been universally selected as this standard; but a diversity of opinion has been entertained as to the temperature at which the gravity of water should be called unity. Hence, whilst our continental neighbours have adopted the freezing temperature, our own countrymen have generally chosen the temperature of 60° Fahr. Water at 60° cannot be a desirable standard, on account of its high rate of expansion at that temperature; and for the same and other reasons the temperature of 32° is not at all more convenient. We conceive that it would be much more philosophical, and lead to many practical advantages, if water at its maximum density were taken as the unit*. In that

* Since this paper was communicated to the Society we have seen the *Annuaire du Bureau des Longitudes* for 1845, in which, under the high authority of Arago, water at its point of maximum density is assumed as the unit for comparison.

case, calculations would often be greatly facilitated; and if the temperature of the water should happen to be a degree under or over the maximum point in any experiment, the extreme slowness of the expansion would avert the possibility of a grave error.

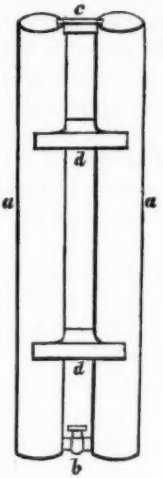
Intending to give still greater accuracy to our future experiments, we deem the present a favourable opportunity for fixing upon a good unit of comparison. We propose therefore to occupy the present series with a brief discussion as to the point of temperature at which water arrives at its state of greatest density.

Although a variety of methods have been employed in the investigation of this subject, they may be classified under two general heads. The first of these embraces all the methods involving the necessity of an accurate acquaintance with the rate of the expansion of some solid body by heat. The inquiry, when made in this way, is one of great difficulty, and has occupied the attention of many of our most accurate experimenters. The Florentine Academicians, Croune, Deluc, Dalton, and others, compared the indications of a thermometer filled with water with one filled with mercury; Lefevre Gineau and Hallström weighed a solid body in water at different temperatures; and Blagden and Gilpin measured the variation of volume by the variation of the weight of water contained in the same vessel at different temperatures.

The other general method does not require a previous acquaintance with the expansion of a solid by heat: it consists virtually in weighing water in water—the heavier water descending, while the lighter ascends to replace it. This principle was introduced by Dr. Hope, who applied it in the following elegant manner:—He filled with water at different temperatures tall glass jars having thermometers at top, middle and bottom. In this way he observed that when water was cooled down to 40° at the surface, it sank to the bottom; and when cooled below 40° at the bottom, it rose again to the surface. Trallés, Count Rumford, Ekstrand and Despretz have repeated Hope's experiment with a similar apparatus.

Believing that the second general method is susceptible of a far greater degree of accuracy than the first, we at once determined to employ it in our own experiments. The particular apparatus of Dr. Hope did not however appear to us to present the method in a form calculated to give results of great accuracy; and hence we have found it necessary to devise a new instrument combining all the theoretical advantages with the requisite facilities for exact observation.

Our instrument is represented in the accompanying sketch. *a a* are two upright vessels of tinned iron, each $4\frac{1}{2}$ feet high and 6 inches in diameter: they are connected at the bottom by means of a brass pipe *b*, furnished with an accurately wrought stop-cock. This pipe is altogether 6 inches long, and enters 1 inch within each vessel. When the stop-cock is opened a clear passage of 1 inch diameter throughout forms a communication between the vessels. A rectangular trough of tinned iron, *c*, 6 inches long, 1 inch broad, and 1 inch deep, forms a communication between the tops of the vessels. In the middle of this trough there is a slide, by means of which the motion of a current along the trough can be stopped when requisite.




The vessels were supported in two places by means of the wooden brackets *d d*, and in order to prevent the greater than desired effect of the atmosphere in raising or depressing their temperature, they were completely covered with haybands. During the experiments the instrument was placed upon a tripod stool resting upon a support quite independent of the floor of the laboratory, in order to keep it entirely free from vibration.

Now if the two vessels be filled with water and made to communicate with one another by opening the stop-cock and removing the slide, it is evident that a current will tend to flow through the trough connecting the tops of the vessels, if the density of the water in one of the vessels be in the least degree greater than that of the water in the other vessel. Although the changes in density are very minute near the maximum point, the extreme mobility of fluids led us to expect that we might in this way arrive at an exact and incontrovertible result.

The *thermometers* employed by us were of extreme accuracy, having been calibrated throughout their whole length, and their delicacy was such as to indicate a change of temperature considerably less than $\frac{1}{100}$th of a degree Fahrenheit. The freezing-points of the thermometers were carefully determined within a few hours of the experiments. Each vessel was furnished with a *stirrer*, consisting of a disc of tinned iron 4 inches in diameter attached to the end of a slender rod

of iron, by means of which the water was thoroughly stirred before each determination of temperature.

In order to measure the motion of the water in the trough connecting the tops of the vessels, a hollow glass ball of about three-eighths of an inch diameter was placed in it. The weight of this glass ball was carefully adjusted so as only just to float: a matter of great importance, as the slightest buoyancy is accompanied by a certain degree of capillary attraction, and makes the ball liable to adhere to the sides of the trough.

The *water* employed in the experiments was distilled by ourselves in clean vessels of tinned iron; and the additional precaution was taken to prevent, as far as possible, the solution of air.

Our method of experimenting was as follows:—Having filled the vessel with distilled water at a temperature of about 37°, we increased the temperature of one of the vessels to 41°·5 by the addition of a small quantity of hot distilled water. We then placed two delicate thermometers upon a proper stand, so that their bulbs dipped in the water to the depth of 6 inches. Having then closed the stop-cock and adjusted the slide, we stirred the water in each vessel thoroughly, and noted the temperatures indicated by the thermometers. The stop-cock was then opened and the slide carefully removed from the trough. After waiting three minutes the glass ball was put into the trough, and its motion watched for two or three minutes with the help of a graduated rule placed at the top of the trough. In conclusion, the stop-cock was again turned, the slide readjusted, the water stirred, and the temperatures again noted. The mean of the temperatures thus observed before and after each trial of the velocity of the current was taken as the temperature of the observation.

The following table contains the results of a series of observations taken in the above manner. The temperature of the laboratory being about 38°, the water in the warmer vessel cooled down more rapidly than the water in the other vessel increased in temperature; and therefore after two or three hours had elapsed, the water in the cooler vessel was found to have acquired greater buoyancy than that in the warmer vessel, although at the commencement of the experiments the current indicated a greater degree of buoyancy in the warmer water.

Series 1.

| Temperature of the water in the warmer vessel. | Temperature of the water in the cooler vessel. | Mean of the temperatures of the two vessels. | Velocity of the current in inches per hour. |
|---|---|---|---|
| 41°·183 | 37°·348 | 39°·265 | 280 from the warmer vessel |
| 41·129 | 37·368 | 39·248 | 240 ditto |
| 40·959 | 37·363 | 39·161 | 20 ditto |
| 40·905 | 37·368 | 39·136 | 8 ditto |
| 40·711 | 37·317 | 39·014 | 40 from the cooler vessel |

We could hardly have anticipated more satisfactory results than those of the above table. They show clearly that while water at a temperature of 40°·905 is lighter than water at a temperature of 37°·368, water at 40°·711 is heavier than water at 37°·317: in other words, that 39°·136 is above, whilst 39°·014 is below the maximum point. By drawing a curve from the results, we find that the exact point of maximum density indicated by the above series of observations is 39°·102.

During the next series of observations the temperature of the laboratory was about 41°, which occasioned a gradual increase of the temperatures of both vessels.

Series 2.

| Temperature of the water in the warmer vessel. | Temperature of the water in the cooler vessel. | Mean of the temperatures of the two vessels. | Velocity of the current in inches per hour. |
|---|---|---|---|
| 40°·742 | 37°·368 | 39°·055 | 22 from the cooler vessel |
| 40·758 | 37·420 | 39·089 | 8 from the warmer vessel |
| 40·773 | 37·470 | 39·121 | 60 ditto |

The point of maximum density indicated by this second series of observations is 39°·078.

Series 3.

| Temperature of the water in the warmer vessel. | Temperature of the water in the cooler vessel. | Mean of the temperatures of the two vessels. | Velocity of the current in inches per hour. |
|---|---|---|---|
| 40°·332 | 37°·633 | 38°·982 | 70 from the cooler vessel |
| 40·402 | 37·682 | 39·042 | 80 ditto |
| 40·425 | 37·709 | 39·067 | 60 ditto |
| 40·440 | 37·745 | 39·092 | 8 ditto |
| 40·448 | 37·791 | 39·120 | 30 ditto |
| 40·467 | 37·837 | 39·152 | 12 from the warmer vessel |
| 40·483 | 37·873 | 39·178 | 30 ditto |

The point of maximum density indicated by the above series will be situated at about 39°·134.

We now proceeded to apply a severer test to our method. In the next series of experiments we arranged matters so that the temperature of the water in one vessel was only a degree and a half higher than that of the other vessel. The expansion of water increasing as the square of the temperature from that of the maximum density, it was obvious that the current in the trough would be much more feeble than in the former experiments. We therefore allowed the vessels to be in perfect repose for six minutes before we introduced the glass ball, and we afterwards watched its motion for four or five minutes.

Series 4.

| Temperature of the water in the warmer vessel. | Temperature of the water in the cooler vessel. | Mean of the temperatures of the two vessels. | Velocity of the current in inches per hour. |
|---|---|---|---|
| 39°·921 | 38°·382 | 39°·151 | 30 from the warmer vessel |
| 39·864 | 38·398 | 39·131 | 0 |
| 39·821 | 38·362 | 39·091 | 0 |
| 39·782 | 38·332 | 39·057 | 2½ from the cooler vessel. |

The position of the point of maximum density according to the above fourth series of experiments will be at 39°·091.

| | | | | | |
|---|---|---|---|---|---|
| I. | Point of maximum density of pure water | | | | 39°·102 |
| II. | ... | ... | ... | ... | 39·078 |
| III. | ... | ... | ... | ... | 39·134 |
| IV. | ... | ... | ... | ... | 39·091 |
| | | | Mean | ... | 39·101 |

Although in the different series of observations there are several irregular results, there is on the whole sufficient consistency among them to enable us to receive 39°·1, the mean of the four sets of observations, as the actual point of maximum density. We think it highly probable that this temperature is within one-hundredth of a degree of the truth: it certainly cannot be more than one-twentieth of a degree in error. We were prevented by the mildness of the season from extending the experiments further, but we doubt not that by repeating them more frequently we should be able to bring the determination of the point to any required degree of accuracy. The result arrived at by Despretz from a very extensive series of experiments, with an apparatus similar to that employed by Hope, is 39°·176 *, which agrees very well

* *Annales de Chimie*, 1839, t. lxx. p. 45.

with our determination. But other results, such as those of Hallström 39°·38, Blagden and Gilpin 39°, Hope 39°·5, Deluc 41°, Lefebvre Gineau 40°, Dalton 38°, Rumford 38°·8, Muncke 38°·804, Stampfer 38°·75, &c., show by their discordance with one another, and their disagreement with our result, the little dependence which can in general be placed on the results of former methods.

We believe that our new method may be applied with great advantage to a variety of interesting problems. One of the most important of these applications is the determination of the dilatation of glass bulbs by heat, which, though formerly presenting great practical difficulties, can now be accomplished in the most simple and decisive manner. The bulb has only to be filled with pure water and reduced successively to two temperatures, one as much above as the other is below the point of maximum density—the rise of the liquid in the stem of course indicates the contraction of the glass in passing from the higher to the lower temperature. The expansion of the glass bulbs being thus accurately ascertained, they may be advantageously applied in determining the dilatations of solutions and other liquids.

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May 4th, 1846.—James Lowe Wheeler, Esq. in the Chair.

C. Binks, Esq. was elected a Member of the Society.

The following papers were read:—

Mr. F. C. Calvert exhibited and described the preparation and composition of the oxides of lead and their combinations with nitric acid and ammonia, which had formed the subject of a series of investigations.

Dr. R. D. Thomson detailed the results of his late investigations on the fattening of cattle.

## CLXX. *Researches upon Cumarine.*

*By* Hermann Bleibtreu.

THE attention of chemists has long been attracted to the *Asperula odorata*, a plant well known in Germany under the name of 'Waldmeister,' and which in many districts, particularly on the Rhine, is employed in the preparation of the favourite 'Maitrank' or 'Maiwein.'

Many experiments have been made for the purpose of separating and investigating the volatile substance contained in the 'Waldmeister,' to which the 'Maiwein' owed its agreeable odour and flavour.

Many years ago Voget * occupied himself with this subject, and obtained from the 'Waldmeister' a crystalline substance, which he described as possessing the same odour as the Tonka bean and *Melilotus*, and which his experiments proved to be benzoic acid.

More lately Kosmann † has published some experiments, which led him to the conclusion that the principle contained in this plant was cumarine, the stearoptine of Tonka beans. By treating the dried plant with alcohol and æther, driving off these solvents and boiling the syrupy residue in water, and evaporating, he obtained a crystalline mass, whose agreeable odour and piquant taste were exactly similar to cumarine prepared from the Tonka beans.

The experiments of Kosmann were however purely qualitative. No analysis was made of the crystals obtained from the Waldmeister, which alone could determine the point; nor was the experiment tried as to the ready transformation of cumarine into salicylic acid, so easily recognised by its action with the salts of the sesquioxide of iron, and from which a tolerable conclusion could have been drawn.

It hence appeared to me desirable to establish by a more exact investigation the observations of Kosmann.

The following experiments instituted for this purpose, and including a revision of the investigation of cumarine by Delalande, were commenced in the laboratory of my friend Professor A. W. Hofmann in Bonn, and finished in that of the Royal College of Chemistry in London, to which I accompanied him in the capacity of assistant on his election as Professor to the latter.

I have much pleasure in embracing this opportunity to express my thanks to Dr. Hofmann for his instructions in organic investigations generally, and more particularly for his assistance in the present memoir.

### *Investigation of the Crystals from* Asperula odorata.

For the preparation of this substance I proceeded in the following manner:—

A quantity of Waldmeister, collected shortly before and during flowering, was dried in the air and digested for some time with spirits of wine; the alcohol was distilled from the dark greenish-brown solution in a water-bath, and the dark

* *Generalbericht des König. Preus. Rhein. Medicinalcol.* Uber das Jahr 1835. Coblenz bei Kehr, page 240.

† *Journ. de Pharm.*, 3 ser. t. v. p. 393. *Ann. der Chem. u. Pharm.*, B. lii. p. 387.

brown residue evaporated to the consistency of syrup. The distilled alcohol had an aromatic odour, and from the last more watery portion small crystalline plates were gradually deposited.

The syrup, boiled with water, and the brown solution separated by filtration from the insoluble matters, consisting of chlorophylle, &c., were agitated with æther. On distilling off the æther there remained a yellow substance, possessing the appearance and odour of honey, from which, after some time, a considerable quantity of yellow crystalline needles separated, which on heating with water to 50° C. collected at the bottom of the vessel into a melted mass, and were dissolved on raising the temperature to the boiling-point. From this solution, which on cooling became milky, crystals of an inch in length were gradually deposited, which were purified by repeated crystallizations. After being thrice recrystallized the crystals were of a pure white colour, but deposited some brownish flakes after melting at a gentle heat. On repeating the recrystallizations a few times more, the substance remained quite unchanged in colour after fusing, and could now be considered as quite pure and proper for analysis.

Before proceeding to the analysis I endeavoured to convert a small portion of the substance into salicylic acid. A few crystals were dissolved in strong potassa ley, evaporated till the yellow colour at first produced had disappeared, and then heated somewhat stronger. The solid residue was saturated with hydrochloric acid and agitated with æther. The æthereal solution, evaporated to drive off the æther, gave with sesquichloride of iron the beautiful violet colour so characteristic of salicylic acid.

*Analysis of the Crystals from* Asperula odorata.

The analysis of the fused crystals, in one case with oxide of copper, in the other with chromate of lead, gave the following results:—

I. 0·3276 grm. gave 0·8821 carbonic acid and 0·1267 water.

II. 0·2607 grm. substance gave 0·7105 carbonic acid and 0·1043 water.

From which the following per-centage is calculated:—

| | I. | II. |
|---|---|---|
| Carbon . . . | 73·63 | 74·33 |
| Hydrogen . . | 4·31 | 4·44 |

According to the experiments of Delalande the formula of

cumarine is $C_{18} H_7 O_4$, giving the following per-centage, which I compare with the mean of his analyses calculated with the new atomic weight of carbon:—

| | Theory. | | Mean of Delalande's experiments. |
|---|---|---|---|
| $C_{18}$ = | 1350·00 | 73·47 | 72·91 |
| $H_7$ = | 87·50 | 4·76 | 4·73 |
| $O_4$ = | 400·00 | 21·77 | |
| | 1837·50 | 100·00 | |

The result of my analyses approach near enough to those of Delalande to prove the identity of cumarine and the substance obtained from the *Asperula odorata*. A comparison however of the amount of carbon and hydrogen shows, particularly in the former, a sufficient deviation to throw a doubt on the absolute number of equivalents. The circumstance likewise of the near agreement, nay even of the excess of the quantity of hydrogen calculated over that obtained in the mean of Delalande's experiments, whilst in analysis the reverse is always the case, gave me grounds to doubt the correctness of his formula, and induced me to repeat the investigation of cumarine obtained from the Tonka beans.

### *Preparation of Cumarine from Tonka Beans.*

The following appeared to be the best method of preparing cumarine from the Tonka beans.

The beans, finely cut or pounded, were digested for some time with strong alcohol. The syrupy mass remaining after distilling off the alcohol, becomes on cooling for the most part a solid magma of crystals of cumarine, which can be easily purified by treatment with animal charcoal and repeated crystallizations. By proceeding in this manner it is more easy to separate a fatty oil, which is contained in considerable quantity in the Tonka bean. This body is colourless, and without any characteristic odour, soluble in æther, insoluble in alcohol and water, and possesses the property of dissolving cumarine in considerable quantity.

The process of treating the beans with æther, or directly extracting the cumarine by boiling in water, is much inferior, as the greater part of the oil is also removed with it, and can afterwards only be separated with difficulty. In the fresh bean the cumarine appears to be contained in solution in this oil, from which it gradually separates in the form of pure white crystals, and is found collected particularly between the cotyledons and on their surfaces under the skin.

*Composition of Cumarine.*

Two combustions of cumarine from the Tonka beans gave the following results:—

I. 0·4870 grm. substance gave 1·3209 carbonic acid and 0·1882 water.

II. 0·6423 grm. substance gave 1·7361 carbonic acid and 0·2416 water.

These numbers correspond in per-centage to

| | I. | II. |
|---|---|---|
| Carbon . . . | 73·97 | 73·72 |
| Hydrogen . . | 4·29 | 4·18 |

These two analyses correspond exactly with that of the cumarine obtained from the *Asperula*. In all there is a larger amount of carbon and a smaller quantity of hydrogen than in the analyses of Delalande.

The expression corresponding to the mean of my experiments is $C_{18} H_6 O_4$, which contains 1 equivalent of hydrogen less than in Delalande's formula, as is seen in the following scheme, in which the experimental and theoretical numbers are compared.

| | Theory. | | Bleibtreu. | Delalande. |
|---|---|---|---|---|
| 18 Carbon . | 1350 | 73·97 | 73·91 | 72·91 |
| 6 Hydrogen | 75 | 4·11 | 4·30 | 4·73 |
| 4 Oxygen . | 400 | 21·97 | | |
| | 1837 | 100·00 | | |

These experiments leave no doubt as to the identity of the crystalline principle of the *Asperula* and the stearoptine of the Tonka bean.

The delightful aroma which characterizes 'Maiwein' is entirely due to this substance. A liquor artificially prepared with the stearoptine of the Tonka bean met with the warmest approbation from a number of the younger teachers in the University of Bonn.

*Products of Decomposition of Cumarine.*

The new formula for cumarine I endeavoured to control by investigating its products of decomposition.

Delalande obtained on heating cumarine with concentrated potassa a peculiar acid, $HO, C_{18} H_7 O_5$, which he described under the name of cumaric acid. According to him, by the continued action of the potassa a further transformation of the latter is effected into that remarkable acid first obtained by Piria as a product of the decomposition of salicine, and to which the attention of chemists has more lately been in the

most lively manner attracted by the investigations of Cahours on the "Oil of the *Gualtheria procumbens.*"

Delalande expresses these transformations by the following formula:—

$$\underbrace{C_{18}H_7O_4+2HO}_{\text{Cumarine.}} = \underbrace{HO,C_{18}H_7O_5+H}_{\text{Cumaric acid.}}$$

$$\underbrace{HO,C_{18}H_7O_5}_{\text{Cumaric acid.}} = \underbrace{HO,C_{14}H_5O_5}_{\text{Salicylic acid.}} + C_4H_2.$$

On repeating the experiments of Delalande I arrived at the following results.

Cumarine dissolves readily in potassa and forms with it a yellowish solution, from which acids precipitate cumarine again unchanged. It is only attacked by heating with concentrated ley, to which pieces of solid caustic potassa have been added. From this solution hydrochloric acid precipitates a substance totally differing in its character from cumarine, and which is evidently the acid described by Delalande.

*By careful treatment of cumarine however by potassa, I have never been able to observe a disengagement of hydrogen.*

The acid prepared in the above manner may contain traces of salicylic acid. After removal of the chloride of potassium and the excess of hydrochloric acid, and dissolving in water, it gave indeed, with salts of the sesquioxide of iron, the violet colour so characteristic of salicylic acid. Delalande however states expressly in his memoir, that this reaction is not only characteristic of salicylic but also of cumaric acid. This remark is evidently erroneous, for on washing with water the acid once crystallized, this reaction became weaker and weaker, and finally totally disappeared on a second crystallization. The violet colour produced by the sesquichloride of iron was consequently due to the presence of a small quantity of salicylic acid, the formation of which cannot easily be prevented.

The acid prepared in the above manner, and freed from salicylic acid as much as possible by repeated recrystallizations, may still contain traces of undecomposed cumarine, from which it must be separated; for this purpose it was dissolved in ammonia. From the yellow solution the excess of ammonia was expelled by boiling, and the yellowish-white silver salt produced by the addition of nitrate of silver was collected on a filter and washed with water, and then with alcohol, and finally æther. After such a treatment the silver salt cannot contain any trace of cumarine, and the acid now separated by hydrochloric acid, extracted by æther, and re-

crystallized from boiling water after distilling off the æther, may be regarded as *pure cumaric acid.*

With salts of sesquioxide of iron it now produces no colour whatever, and possesses the following properties. It is readily soluble in alcohol and æther, and crystallizes from boiling water in white brittle crystals. It possesses a decidedly acid reaction, and expels carbonic acid from its salts. Its point of fusion is near 190° C. If more strongly heated, it is partly decomposed into white shining crystals, which sublime, and a brownish residue.

The cumarate of ammonia is not precipitated by a salt of baryta; but a white powdery insoluble precipitate is obtained by the addition of acetate of lead.

A combustion with chromate of lead of cumaric acid dried at 100° C. gave the following results:—

0·3415 grm. of substance gave 0·8215 carbonic acid and 0·1532 water.

In per-centage,—

| | |
|---|---|
| Carbon . . . . . | 65·61 |
| Hydrogen . . . . | 4·98 |

These numbers correspond exactly to the formula of Delalande for this acid, HO, $C_{18} H_7 O_5$.

The following are the experimental and theoretical numbers:—

| | Theory. | | Bleibtreu. | Delalande. |
|---|---|---|---|---|
| 18 Carbon . | 1350·00 | 65·85 | 65·61 | 65·34 |
| 8 Hydrogen | 100·00 | 4·88 | 4·98 | 5·05 |
| 6 Oxygen . | 600·00 | 29·27 | | |
| | 2050·00 | 100·00 | | |

To control this formula I also analysed the same silver salt as Delalande. It was obtained, as above stated, by dissolving cumaric acid in ammonia and precipitating with nitrate of silver. There appeared however to exist two compounds of cumaric acid with oxide of silver; for on precipitating a solution of the acid in excess of ammonia a flocculent orange-yellow precipitate was obtained, whilst that from the neutral salt was light yellow, almost white, quickly settling to the bottom of the vessel. The two compounds are further essentially distinguished by the orange-coloured substance becoming quickly brown on exposure to the air, and being immediately decomposed on heating to 100° C., whilst under the same circumstances the lighter remains quite unchanged. In the following analyses the latter compound was employed.

I. 0·5850 grm. cumarate of silver gave 0·8580 carbonic acid and 0·1392 water.

In per-centage,—

| | |
|---|---|
| Carbon . . . . . | 40·00 |
| Hydrogen . . . . | 2·64 |

II. 0·8237 grm. of the salt gave 0·3287 silver.
III. 0·5181 grm. salt gave 0·2049 silver.
In per-centage,—

| | |
|---|---|
| II. Silver . . . . | 39·90 |
| III. Silver . . . . | 39·55 |
| Mean number . | 39·72 |

These results correspond exactly with those of Delalande and give the following formula, $AgO, C_{18} H_7 O_5$. The calculated and experimental numbers are as follows:—

| | Theory. | | Experimental. | |
|---|---|---|---|---|
| | | | Bleibtreu. | Delalande. |
| 18 C . | 1350·00 | 39·86 | 40·00 | 39·82 |
| 7 H . | 87·50 | 2·58 | 2·64 | 2·62 |
| 6 O . | 600·00 | 17·72 | | |
| 1 Ag . | 1349·00 | 39·84 | 39·72 | 40·00 |
| | 3386·51 | 100·00 | | |

*Formation of Cumaric and Salicylic Acid from Cumarine.*

From the above experiments it is evident that the formula given by Delalande to cumaric acid must be regarded as the correct one. The representation however of the formation of this acid, to which this chemist was led by the incorrect formula of cumarine, requires correction. The formation of cumaric acid depends upon no decomposition of water, the oxygen of which is added to the elements of cumarine, but simply on the assumption of 2 equivalents of this body, exactly analogous to the formation of benzilic acid from benzil, or isatinic acid from isatine.

$$\underbrace{C_{28} H_{10} O_4 + 2HO}_{\text{Benzil.}} = \underbrace{HO, C_{28} H_{11} O_5}_{\text{Benzilic acid.}}$$

$$\underbrace{C_{16} H_5 NO_4 + 2HO}_{\text{Isatine.}} = \underbrace{HO, C_{16} H_6 NO_5}_{\text{Isatinic acid.}}$$

$$\underbrace{C_{18} H_6 O_4 + 2HO}_{\text{Cumarine.}} = \underbrace{HO, C_{18} H_7 O_5}_{\text{Cumaric acid.}}$$

It is not requisite even to fuse the cumarine with caustic potash: by the employment of an alcoholic solution of potassa it is also transformed, though very slowly, into cumaric

acid. There however in this latter case always remains, even after long treatment, a large portion of cumarine undecomposed.

The evolution of hydrogen mentioned by Delalande, and which, as already stated, I never observed in a well-conducted experiment, arose evidently from the formation of salicylic acid by the further action of the potassa on the cumaric acid. This view is supported by the violet-coloured reaction of sesquichloride of iron described by him, and which, as I have shown, does not belong to cumaric acid. His cumaric acid evidently contained a small quantity of salicylic acid.

From the aforesaid grounds, the view taken by Delalande on the transformation of cumaric into salicylic acid must also be modified. According to him, no evolution of hydrogen takes place in this formation, but an aromatic gas is disengaged burning with a coloured flame, and which he regarded as a carbo-hydrogen $C_4 H_2$, representing the difference of constitution between the two acids—

$$\underbrace{HO, C_{18} H_7 O_5}_{\text{Hydrated cumaric acid.}} - \underbrace{C_4 H_2}_{\text{Aromatic gas.}} = \underbrace{HO, C_{14} H_5 O_5}_{\text{Hydrated salicylic acid.}}.$$

This manner of viewing the reaction is evidently incorrect. If pure cumarine is fused with hydrate of potassa, the latter is almost entirely transformed into carbonate after the formation of the salicylic acid. The carbon therefore separates in the form of an oxygenated compound.

I have made no quantitative experiment on this point; but all my observations tend to prove that the formation of the salicylic acid may be represented by the following equations:—

$$\underbrace{HO, C_{18} H_7 O_5}_{\text{Cumaric acid.}} + 8HO = \underbrace{HO, C_{14} H_5 O_5}_{\text{Salicylic acid.}} + 4CO_2 + 10H.$$

As to the aromatic gas burning with a brilliant flame, which is evolved in the latter stages, it is no carbo-hydrogen, but the oxide of a carbo-hydrogen, viz. hydrate of phenyl, arising from the further loss of carbonic acid from the salicylic acid already formed,—

$$\underbrace{HO, C_{14} H_5 O_5}_{\text{Salicylic acid.}} - 2CO_2 = \underbrace{HO, C_{12} H_5 O}_{\text{Hydrate of phenyl.}}.$$

### *Nitrocumarine.*

Delalande has studied the action of nitric acid on cumarine. The correction of the formula of the latter body made it desirable to repeat this experiment also, as it was probable

that a corresponding change would likewise require to be made in that of the product of decomposition.

Cumarine dissolves without almost any evolution of red fumes in cold fuming nitric acid, and with considerable elevation of temperature. On addition of water a white cheesy precipitate is obtained, which quickly settles to the bottom. The fluid possesses a deep yellow colour. After washing with cold water, the precipitate was dissolved in boiling alcohol, from which, on cooling, white shining silky crystals separated. In this treatment with nitric acid a strong heat is to be particularly avoided, as the whole of the cumarine is converted into nitropicric acid if the fluid is allowed to boil. The formation of a small quantity of the latter acid can never be completely avoided, and from this cause arises the yellow colour of the mother-liquor.

To the above product of decomposition Delalande gave the name nitrocumarine, and the following formula derived from his view of the composition of cumarine:—

$$C_{18}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_4.$$

It is scarcely necessary to remark that this formula must be changed into

$$C_{18}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}O_4,$$

as is shown by the analysis of the fused crystals with oxide of copper.

0·5675 grm. of substance gave 1·1657 carbonic acid and 0·1348 water.

In per-centage,—

| | |
|---|---|
| Carbon . . . . . | 56·02 |
| Hydrogen . . . . | 2·64 |

which, compared with the per-centage calculated from the new formula, is

| | Theory. | | Experiment. |
|---|---|---|---|
| 18 Carbon . | 1350·00 | 56·54 | 56·02 |
| 5 Hydrogen | 62·50 | 2·62 | 2·64 |
| 1 Nitrogen . | 175·25 | 7·34 | |
| 8 Oxygen . | 800·00 | 33·50 | |
| | 2387·75 | 100·00 | |

Delalande's formula requires the following per-centage:—

| | |
|---|---|
| Carbon . . . . | 56·24 |
| Hydrogen . . . | 3·12 |

The determination of the hydrogen, on which the formula more directly depended, leaves no doubt as to the choice of the two. The formation of nitrocumarine is analogous to that of nitrobenzol, nitrostyrol, &c.:—

$$\underbrace{C_{18}H_6O_4}_{\text{Cumarine.}}+HO,NO_5=\underbrace{C_{18}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}O_4}_{\text{Nitrocumarine.}}+2HO.$$

I have but little to add to Delalande's description of the properties of this body. Nitrocumarine dissolves with difficulty in water, alcohol and æther, and crystallizes in fine needles from these solvents as soon as the temperature falls a little below their boiling-point. Its point of fusion is about 170° C.; heated beyond this it sublimes without decomposition in the form of large white crystals of the lustre of mother-of-pearl.

Nitrocumarine forms with alkalies a solution of a deep yellow, almost red colour, which disappears on the addition of an acid, with separation at the same time of a white crystalline matter. This reaction was further examined in the hopes of obtaining an acid corresponding to nitrocumarine, viz. the nitrocumaric acid.

For this purpose nitrocumarine was boiled for some time in an alcoholic solution of potassa; the potassa compound formed, decomposed by hydrochloric acid, and the precipitate after removal by washing of the chloride of potassium, recrystallized from boiling alcohol.

To free the crystals (which I regarded as nitrocumaric acid) from any nitrocumarine which might still be mixed with them, they were dissolved in ammonia, and on boiling, to remove any excess of the latter, a portion of the substance was deposited in the form of white crystalline flakes. That these crystals were only cumarine was proved by the absence of any trace of ammonia on heating with potassa.

The filtered solution, which was neutral, gave with nitrate of silver a beautiful orange-yellow colour, with acetate of lead an orange precipitate. Both compounds were soluble in a considerable quantity of water, forming a lightish yellow solution, but less so in alcohol and æther; so that they could be purified by boiling in these menstrua. I have analysed these compounds as well as the substance separated from them by acids.

The lead and silver precipitates are direct compounds of nitrocumarine with the oxides of the metals, and the electronegative bodies obtained from them is *pure nitrocumarine.*

The combustion of this substance with oxide of copper gave the following results:—

0·2567 grm. of substance gave 0·5338 carbonic acid and 0·0672 water.

In per-centage,—

| | |
|---|---|
| Carbon . . . . | 56·71 |
| Hydrogen . . . | 2·90 |

Nitrocumarine, $C_{18}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}O_4$, contains, as before stated,

| | |
|---|---|
| Carbon . . . . | 56·54 |
| Hydrogen . . . | 2·62 |

whilst nitrocumaric acid, HO, $C_{18}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_5$, corresponding to cumaric acid, ought to contain the following widely differing per-centage,—

| | |
|---|---|
| Carbon . . . . | 51·67 |
| Hydrogen . . . | 3·35 |

The lead compound was dried at 100°, decomposed by nitric, and precipitated by dilute sulphuric acid.

0·6557 grm. substance gave 0·5548 sulphate of lead.

In per-centage,—oxide of lead 62·27, which would give a formula approaching nearly to

$$3PbO, C_{18}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}O_4,$$

of which the calculated per-centage of lead is 63·66.

The silver compound being decomposed by the temperature of the water-bath was dried *in vacuo*.

A determination of the silver made by burning the compound, in which however a slight loss was incurred through deflagration, gave in 0·3037 grm. of substance 0·1526 silver.

In per-centage,—oxide of silver 53·97, which corresponds to a compound for nitrocumarine and 2 equivalents of oxide of silver,

$$2Ag_2O, C_{18}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}O_4,$$

of which the per-centage of oxide of silver calculated would be 54·83.

From these experiments it is evident that nitrocumarine undergoes no decomposition on boiling in an alcoholic solution of potassa. The same lead and silver compounds are also obtained by adding a lead or silver salt to nitrocumarine simply dissolved in ammonia. Further experiments must

decide whether nitrocumaric acid can be obtained by careful fusion with caustic alkalies, or directly from cumaric acid, by proper treatment with nitric acid.

The formation of this acid would have been of some interest. The late investigations of Zinin have shown us that acids of this class, under the influence of reducing agents, as hydrosulphuric acid, &c., exchange 4 equivalents of oxygen for 2 of hydrogen, or, to express it otherwise, 1 equivalent of hyponitric acid for 1 of amidogen.

Whilst bases are thus formed from nitro-carbohydrogens, the electro-negative character of the nitro-acids remains unchanged. Benzoic acid, for example, treated in the above manner, gives the following series:—

Benzoic acid . . $HO, C_{14} H_5 O_3$

Nitrobenzoic acid. $HO, C_{14}\left\{\begin{matrix} H_4 \\ NO_4 \end{matrix}\right\} O_3$

Amidobenzoic acid / Benzamidic acid $\Big\}$ $HO, C_{14}\left\{\begin{matrix} H_4 \\ Ad \end{matrix}\right\} O_3$

Were it possible to form from cumaric acid a similar series:

Cumaric acid . . $HO, C_{18} H_7 O_5$

Nitrocumaric acid. $HO, C_{18}\left\{\begin{matrix} H_6 \\ NO_4 \end{matrix}\right\} O_5$

Amidocumaric acid $HO, C_{18}\left\{\begin{matrix} H_6 \\ Ad \end{matrix}\right\} O_5$.

it gave a hope of producing artificially hippuric acid, for amidocumaric acid is, according to its formula, nothing but hippuric acid:

$$\underbrace{HO, C_{18}\left\{\begin{matrix} H_6 \\ Ad \end{matrix}\right\} O_5}_{\text{Amidocumaric acid.}} = \underbrace{HO, C_{18} H_8 NO_5}_{\text{Hippuric acid.}}.$$

Whether or not such a relation exists must be decided by further experiments, which I intend still to make in this direction. In the following I will briefly state some experiments made partly with the same intention, and which as yet have not led to decided results.

It was not impossible that by the direct action of reducing agents on nitrocumarine an amidocumarine could have been formed, which by treatment with alkalies might have been converted into the desired acid. For this purpose a quantity of nitrocumarine was mixed with alcohol, into which ammoniacal gas was passed till the whole was dissolved, and then submitted for a considerable time to a current of hydrosulphuric acid.

The fluid, from which, even after several days, no sulphur separated, was distilled in a retort till no more sulphide of ammonia passed over. On exposure to the air in a flat vessel it now deposited a yellow, slimy, tenacious mass, the characteristic garlic smell of which led to the suspicion of its containing sulphur.

By longer exposure to the air the slimy mass assumed the consistence of wax, and finally hardened into a resinous-like body, insoluble in water, but tolerably soluble in alcohol and æther.

Ammonia also dissolves this substance with separation of a little sulphur. On boiling this solution a portion of the substance is again deposited as the ammonia is driven off.

The filtered solution, which is nearly neutral, gave on the addition of hydrochloric acid a brown-coloured amorphous precipitate, and with lead and silver salts light yellow compounds.

Want of substance has as yet prevented me from making a thorough investigation of these bodies. I will however here only add, that the yellow lead compound gave 34·21 per cent. of lead, and that the organic substance separated from it contained 9·55 per cent. of sulphur.

### *Cumarine in* Anthoxanthum odoratum.

The detection of cumarine in the *Asperula odorata* led to the suspicion that this principle is probably also contained in other plants in which benzoic acid has been hitherto supposed to have been found.

Some time ago Guillemette * showed that the crystalline principle of the *Melilotus officinalis*, which was formerly believed to be benzoic acid, was identical with cumarine.

This observation was completely confirmed by some experiments made by me with the crystalline principle of this plant, particularly by completely transforming it into salicylic acid.

Of the other plants said to contain benzoic acid I have as yet been able to obtain only *Anthoxanthum odoratum*, a grass to which is attributed the agreeable smell of new hay, and which, under the name of 'Ruchgras,' is to be found in most meadows.

To detect the cumarine I proceeded in the same manner as with the *Asperula odorata*, and obtained white crystals, which in odour and taste, as well as in all other properties, were not

* *Ann. der Chem. u. Pharm.*, B. xiv. p. 324. *Journ. de Pharm.*, 1835, p. 172.

to be distinguished from cumarine. On fusing these crystals with hydrate of potassa and testing the product of decomposition with sesquichloride of iron, the intense violet colour produced by the salicylic acid which had been formed showed with certainty the presence of cumarine in the original substance.

The hippuric acid found in the urine of graminivorous animals has in various ways been supposed to be derived from the benzoic acid imagined to exist in the *Anthoxanthum odoratum*. The transformation experienced by that acid in the animal œconomy appeared in the highest degree to give support to this view.

It would be desirable to try if the same change takes place with cumarine. The narcotic action of this substance on the animal organism however prevented the making of any direct experiments.

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## CLXXI. *On the Solvent Action of Drainage-Water on Soils.* By John Wilson, *Esq.*

IN the autumn of 1844, being a resident in East Lothian, where the system of *thorough draining* is very extensively carried out, it occurred to me that the drainage-water during its percolation of the soil must necessarily dissolve out and carry away a great portion of the soluble constituents of it, which, by the practice as at present followed, are carried off the land and entirely lost to the farmer. I therefore took advantage of the first fall of rain sufficient to set the drains running after the dry weather of the autumn, and collected some of the drainage-water, which I subjected to a partial analysis, the particulars of which were described in a paper read by Dr. W. Gregory at a meeting of the Royal Society, Edinburgh, in the early part of last year. The results I then obtained, though very incomplete, were quite sufficient to show me that they had a very important bearing on agriculture, and to induce me to go on with their further investigation.

About the usual quantity of rain had fallen during the time between November, when I collected the first sample, and April 29th, when I obtained the second, and during the whole of that period the land had laid ploughed as a winter fallow.

Immediately after the second sample was taken the field was prepared for seed and sown with guano and barley. In a few days after (May 16th) I was enabled to collect a third sample (of course from the same drains), and having submitted them to analysis, the following are the results:—

*Second Sample.*—18 lbs. of drainage-water on evaporation gave 15·2 grs. of solid residue, or about ·844 gr. to the pound.

| | |
|---|---|
| Organic matter and water in combination | 3·4 |
| Silica | 0·9 |
| Silicate of alumina | 0·4 |
| Chloride of magnesium | 1·12 |
| Chloride of sodium | 1·8 |
| Chloride of calcium | 3·0 |
| Sulphate of alumina | 0·85 |
| Peroxide of iron | 2·1 |
| Phosphate of lime | 0·3 |
| | 13·87 |

*Third Sample.*—18 lbs. of drainage-water on evaporation gave 27·5 grs. of solid residue, or about 1·525 gr. to the pound.

| | |
|---|---|
| Organic matter, &c. | 7·8 |
| Silica | 0·7 |
| Silicate of alumina | 0·2 |
| Peroxide of iron | 2·25 |
| Phosphate of magnesia | 1·8 |
| Magnesia ? | 1·69 |
| Chloride of sodium | 2·615 |
| Chloride of calcium | 2·107 |
| Carbonate of lime | 2·7 |
| Phosphate of lime | 3·1 |
| Phosphate of alumina | 0·45 |
| | 25·412 |

I should here observe that the first sample, collected in November, after the drains had been dry for many weeks previous, contained 2·25 grs. of solid residue to the pound; whereas that collected in the following April (No. 2), after the land had been continually drenched by the winter's rains, only gave ·844 gr. to the pound.

On adding a quantity of easily soluble manure (guano) to the soil, the first waters (No. 3) that passed through not only brought with them an increased quantity (1·525 gr. to the pound), but they contained many of the very ingredients that constituted the value of the manure itself.

At the time the paper referred to was read at the Royal Society, Edinburgh, it was suggested that possibly the turbid portion first discharged from the drains after heavy rains might contain matter also very valuable to the soil; but on comparing the subjoined analysis with that of *the drained soil*, it appears to be composed of the same ingredients, with a decrease in the proportion of silica and an increase in the lime, both of which may be readily accounted for.

*Analysis of Soil deposited from Turbid Drain-Water.*

| | |
|---|---|
| Silica . . . . . | 60·0 |
| Silicate of alumina . . . . | 17·5 |
| Protoxide of iron . . . . | 6·5 |
| Sulphate of lime . . . . | 9·4 |
| Sulphate of magnesia . . . | 0·75 |
| Phosphate of lime . . . . | 0·6 |
| Alumina . . . . . | 4·0 |
| Water, &c. . . . . | 1·25 |
| | 100·00 |

I do not for a moment wish to question the value of the principle of *thorough draining*; that is now I believe universally admitted; but if its results are deemed so beneficial to the farmer under the present practice, how much more so would they not become, if some remedy were devised either to prevent as much as possible this great abstraction, or else to render the enriched drainage-water again available to the soil!

This subject has not, I find, escaped the observant mind of Liebig, and in fact forms the basis of the 'Patent Manure,' according to his specification in October last. He has argued theoretically to the same end, and has proffered a remedy in the shape of a manure, by his patent process rendered much less soluble than before, which of course would not be acted upon so readily by the percolating rain-water, and would consequently remain longer in the soil for the purposes of vegetation.

Mr. Smith of Deanston, a man to whom practical agriculture is deeply indebted, has suggested the application of all manures whatsoever in a largely diluted liquid state, and which I am informed has been most successfully applied on the western coast of Scotland.

Now both of these plans will most assuredly tend to lessen the loss at present sustained; the one by diminishing the solubility of the manures employed, and the other by rendering the drainage-water again available.

But should the farmer object to take advantage of either plan, it would appear expedient to avoid using as much as possible the very soluble manures, and instead of giving his land the usual good dose of manure that is expected to suffice for two or three seasons, to divide the quantity, and to apply it in as small a proportion and as frequently as the nature of his crops will permit him to do. In such case his crops will get more and his ditches less than by the present practice.

May 18, 1846.—The President in the Chair.

John Blyth, M.D., was elected an Associate of the Society.

The following papers were read:—

## CLXXII. *On Palmic Acid, a Fat Acid related to the Margaryl Series.* *By* Lyon Playfair, *Esq., Ph.D.*

BOUDET* has shown that castor oil is solidified by nitric acid containing peroxide of nitrogen ($NO_4$), and that the latter is itself sufficient for this purpose. He described the solid fat thus procured under the name of *palmin*, and the fat acid obtained by the decomposition of its soap as *palmic acid.*

Palmic acid is stated to have a fusing-point of 50° C., although described as usually having it a few degrees lower; but I have never succeeded in procuring it of a higher melting-point than 45° to 46° C. (113° to 114° F.). Boudet did not analyse this acid, nor has it, as far as I am aware, engaged the attention of any other chemist. The singular nature of the compound formed merits a careful examination; so without assigning to myself the task of determining at present the reason of the transformation, I propose to examine the composition of palmin and palmic acid.

Palmin, as well as castor oil, contains glyceril, as has previously been asserted by Bussy, Lecanu and Boudet, but the solidification of the oil is not due to the presence of this compound. In order therefore to be more assured of the purity of the acid formed, I operated principally upon the acids of castor oil. For this purpose, castor oil is saponified by caustic soda and the soap separated by common salt. The soap removed from the liquor is redissolved in pure water and again separated by salt; and this operation is repeated until the excess of caustic soda is removed. The soap is now quite white and readily soluble in hot water, from which solution the fatty acids are separated by the addition of muriatic acid. They are of a pale-olive colour, and are purified from adhering muriatic acid by repeated washings with water.

The acids thus procured are mixed with diluted nitric acid, through which is passed a stream of peroxide of nitrogen, made by the action of nitric acid on starch. The acids, which are previously fluid, soon become solid, and finally acquire the colour and consistence of pale yellow bees'-wax. This solid substance is washed with hot water till all the nitric acid is removed, the washing being performed by melting it in hot water, and drawing off the latter by a siphon. This fat is not *palmin*, but the acid contained in that substance; it differs

* *Annales de Chimie et de Physique*, t. l. p. 411.

from palmin by not containing glycerin. Thus prepared, it is readily soluble in alcohol, which on evaporation yields palmic acid of a yellow colour and still very impure. It is purified by repeated crystallizations and pressure, and when quite pure has a melting-point between 113° to 114° F. There remains in the alcohol an uncrystallizable yellow oil, which becomes red on being saponified with caustic potash.

Palmic acid, procured as described, is readily soluble in alcohol, from which it crystallizes, the crystals generally being grouped together into clumps. From a fused state it solidifies into stars, consisting of small crystals radiating from a centre. The acid was burned with oxide of copper, and gave the following results:—

I. 0·074 grm. gave 0·2005 grm. carbonic acid, and 0·079 water.

II. 0·128 grm. gave 0·3455 grm. carbonic acid, and 0·1365 grm. water.

| | I. | II. | Mean. |
|---|---|---|---|
| Carbon . . . . | 73·89 | 73·61 | 73·75 |
| Hydrogen . . | 11·86 | 11·84 | 11·85 |
| Oxygen . . . | 14·25 | 14·55 | 14·28 |
| | 100·00 | 100·00 | 100·00 |

In order to determine the atomic weight of the acid, the silver salt was prepared in the following manner:—The pure acid was boiled with a strong solution of pure carbonate of potash, which it readily decomposes: on cooling, the soap separated and was removed; it was then dried and dissolved in alcohol; the solution of soap, after being separated from the carbonate of potash, was filtered and evaporated to dryness in a water-bath; it was then dissolved in warm water and precipitated by an excess of nitrate of silver, the precipitate being washed in the dark.

Thus prepared, palmate of silver is a light white powder, insoluble in alcohol and æther, but readily soluble in ammonia. The following determinations of the amount of silver give the data for estimating the atomic weight.

I. 0·994 grm. salt left on ignition 0·271 silver.
II. 0·315 grm. salt left 0·0855 grm. silver.
III. 0·3195 grm. salt left 0·0885 grm. silver.

| | | |
|---|---|---|
| I. | Silver = 27·26 | per cent. |
| II. | ... 27·14 | ... |
| III. | ... 27·69 | ... |
| Mean . . . | 27·36 | ... |

This makes for the atomic weight of the silver salt 4937, and for that of the acid contained in it, 3486.

The silver salt burned with oxide of copper gave the following results:—

I. 0·395 grm. gave 0·751 carbonic acid, and 0·303 water.

II. 0·2590 grm. gave 0·5005 carbonic acid, and 0·192 water.

III. 0·2990 grm. gave 0·5770 carbonic acid, and 0·2190 water.

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . . . | 51·64 | 52·66 | 52·64 |
| Hydrogen . . | 8·52 | 8·23 | 8·12 |
| Oxygen . . . | 12·48 | 11·75 | 11·88 |
| Silver . . . . | 27·36 | 27·36 | 27·36 |

From these data the following theoretical composition is calculated:—

| | | In 100 Parts. |
|---|---|---|
| 34 Carbon . . . . | 2550 | 52·05 |
| 32 Hydrogen . . | 400 | 8·16 |
| 6 Oxygen . . . | 600 | 12·26 |
| 1 Silver . . . . | 1349 | 27·53 |
| | 4899 | |

Hence the theoretical composition of the anhydrous acid is,

| | | In 100 Parts. |
|---|---|---|
| 34 Carbon . . . . | 2550 | 73·91 |
| 32 Hydrogen . . | 400 | 11·59 |
| 5 Oxygen . . . | 500 | 14·50 |
| | 3450 | |

This agrees closely with the numbers found in the analysis of the acid, showing that it is anhydrous, and possesses the formula $C_{34} H_{32} O_5$.

I remarked that the acid obtained by saponifying palmin had a melting-point which never exceeded 112°, while the acid prepared directly by crystallizing the solidified fatty acids without saponification possessed a melting-point 2° higher. To ascertain whether any change took place upon saponification, a portion of pure palmic acid, procured as formerly described, was saponified by potash, liberated by hydrochloric acid, crystallized out of alcohol and analysed. Its melting-point was 111°·5 F.

I. 0·1575 grm. acid gave 0·414 carbonic acid, and 0·1635 water.

II. 0·166 grm. substance gave 0·4345 carbonic acid, and 0·171 water.

III. 0·0805 grm. substance gave 0·2115 carbonic acid, and 0·0835 water.

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . . . | 71·68 | 71·26 | 71·65 |
| Hydrogen . . | 11·53 | 11·44 | 11·52 |
| Oxygen . . . | 16·79 | 17·30 | 16·83 |
| | 100·00 | 100·00 | 100·00 |

Hence the acid has altered in composition during saponification. A silver salt was now prepared in the manner previously described.

0·3195 grm. substance left on ignition 0·0885 silver.

0·1785 grm. substance, burned with oxide of copper, gave 0·3425 carbonic acid, and 0·133 water.

| | | | | In 100 Parts. |
|---|---|---|---|---|
| Carbon . . . . | 52·33 | 34 | 2550 | 52·05 |
| Hydrogen . . | 8·28 | 32 | 400 | 8·16 |
| Oxygen . . . | 11·70 | 6 | 600 | 12·26 |
| Silver . . . . | 27·69 | 1 | 1349 | 27·53 |
| | 100·00 | | 4899 | 100·00 |

The silver salt is therefore of the same composition as that made from the acid analysed before saponification. The only alteration is in the assumption of an atom of water during the separation from the soap, as will be seen from the following theoretical composition:—

| | | In 100 Parts. |
|---|---|---|
| 34 Carbon . . . . | 2550 | 71·57 |
| 33 Hydrogen . . | 412·5 | 11·57 |
| 6 Oxygen . . . | 600·0 | 16·96 |
| | 3562·5 | 100·00 |

Hence the palmic acid procured by decomposing palmate of potash differs only in its assumption of an atom of water. Its formula is $HO, C_{34} H_{32} O_5$, the water being displaced by oxide of silver during the formation of the silver salt.

*Palmate of Lead.*—A solution of palmate of potash poured into a solution of acetate of lead causes the precipitation of a basic salt, which was analysed, but appears to be of no definite composition.

*Palmate of Barytes.*—This salt was made by precipitating palmate of potash with chloride of barium, and washing the precipitate first with water, then with alcohol. It is a white powder with a soapy feeling to the touch; it is insoluble in water.

0·391 grm. of the salt yielded 0·1275 sulphate of barytes.

0·547 grm. salt, burned with chromate of lead, gave 1·164 carbonic acid, and 0·448 water.

| | | | | In 100 Parts. |
|---|---|---|---|---|
| Carbon . . . . | 58·04 | 34 | 2550 | 57·86 |
| Hydrogen . . | 9·09 | 33 | 400 | 9·08 |
| Oxygen . . . | 11·42 | 5 | 500 | 11·35 |
| Barytes . . . | 21·45 | 1 | 957 | 21·71 |
| | 100·00 | | 4407 | 100·00 |

*Palmic Æther.*—This æther was prepared by dissolving hydrated palmic acid in hot alcohol and then passing through the solution a stream of hydrochloric acid gas. Water is then added, and the æther washed with hot water. When the æther is thoroughly washed, the water is allowed to cool, and the æther solidifies into a crystalline mass which is easily removed. It fuses at 61° F., and is very soluble in hot alcohol, but sparingly so in cold. Burned with oxide of copper it gave the following results:—

I. 0·126 grm. substance gave 0·335 carbonic acid, and 0·1385 water.

II. 0·070 grm. substance gave 0·1855 carbonic acid, and 0·076 water.

III. 0·129 grm. gave 0·345 carbonic acid, and 0·141 water. The specimen analysed in this case was further purified by crystallization in alcohol.

| | I. | II. | III. | | | In 100 Parts. |
|---|---|---|---|---|---|---|
| Carbon . . . . | 72·51 | 72·27 | 72·93 | 38 | 2850·0 | 72·85 |
| Hydrogen . . | 12·22 | 12·05 | 12·13 | 37 | 462·5 | 11·82 |
| Oxygen . . . | 15·37 | 15·68 | 14·94 | 6 | 600·0 | 15·33 |
| | 100·00 | 100·00 | 100·00 | | 3912·5 | |

The acid is therefore united with one equivalent of æther, its formula being $C_4 H_5 O, C_{34} H_{32} O_5$.

*Palmin.*—It now only remained to determine the composition of *palmin* itself. For this purpose palmin was prepared by allowing castor oil to stand in contact with dilute nitric acid containing peroxide of nitrogen until it solidified. The solid fat was purified by repeated solutions in æther, in which it is very soluble, although only sparingly so in cold alcohol. It deposits itself from the æthereal solution in opaline grains without the appearance of crystallization, and has the melting-point at 43° C. (109° F.).

I. 0·0865 grm. substance burned with oxide of copper gave 0·231 carbonic acid, and 0·089 water.

II. 0·123 grm. substance gave 0·3295 carbonic acid, and 0·128 water.

| | I. | II. | | | In 100 Parts. |
|---|---|---|---|---|---|
| Carbon . . . . | 72·84 | 73·06 | 37 | 2775 | 73·02 |
| Hydrogen . . | 11·43 | 11·56 | 34 | 425 | 11·18 |
| Oxygen . . . | 15·73 | 15·38 | 6 | 600 | 15·80 |
| | 100·00 | 100·00 | | 3800 | 100·00 |

This empirical formula leads us to the following rational one:—

| | C. | H. | O. |
|---|---|---|---|
| Palmic acid . . . . . | 34 | 32 | 5 |
| Oxide of lipyle . . . | 3 | 2 | 1 |
| Palmin . . . . . | 37 | 34 | 6 |

Had this acid possessed one atom more hydrogen, that is, if the analyses warranted us in assuming 33 atoms of hydrogen instead of 32, the acid would have become one of the members of the margaryle series, assuming as correct the formula given to it by Redtenbacher.

| | |
|---|---|
| Margaric acid . . . . . | $C_{34} H_{33} O_3$ |
| Palmic acid (assumed formula) | $C_{34} H_{33} O_5$ |
| Stearic acid . . . . . | $2(C_{34} H_{33}) O_5$ |

But the analyses do not warrant us in this assumption; and we are therefore compelled to adopt $C_{34} H_{32} O_5$ as the formula of palmic acid.

Now Berzelius, Dumas and Mulder argue that margaryl, the radical of margaric and stearic acids, possesses another equivalent of hydrogen, being in fact $C_{34} H_{34}$. In this case, palmic acid connects itself with margaric acid in a very interesting way. Palmic acid, $C_{34} H_{32} O_5$, may in fact be viewed as margaric acid, $C_{34} H_{34} O_3$, in which two atoms of hydrogen have become replaced by two atoms of oxygen.

| | |
|---|---|
| Margaric acid . . . | $C_{34} H_{32} H_2 O_3$ |
| Palmic acid . . . . | $C_{34} H_{32} O_2 O_3$ |

I previously pointed out a similar case of substitution in œnanthic and myristic acids*.

| | |
|---|---|
| Myristic acid . . . | $C_{28} H_{27} O_3$ |
| Œnanthic acid . . . | $C_{28} H_{26} O_4$ |

The substitution in this case of an equivalent of oxygen for one of hydrogen is exactly the same as with palmic and margaric acids, and seems to show that such relations are not merely fortuitous.

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## CLXXIII. *On the Compounds of Phosphoric Acid with Aniline.* By Edward Chambers Nicholson, *Esq.*

OF the inorganic acids there is none so remarkable for the number and variety of the compounds it forms with bases as phosphoric acid. The peculiar and complex reactions of the salts of this acid were first satisfactorily explained by Prof.

* *Annalen der Chemie*, Bd. xxxvii. S. 155.

Graham, in his well-known paper published in 1833*. The modifications of phosphoric acid by its amount of water of hydration, giving rise to pyrophosphoric and metaphosphoric acid, beautifully explained all that was enigmatical in the observed reactions.

Prof. Graham's excellent experiments have added a great deal to our knowledge of phosphoric acid; the study, however, of this acid and its salts is by no means exhausted. I consequently hope that any contribution to the subject will be accepted.

The following experiments, which were instituted in the laboratory of the Royal College of Chemistry, relate to the combination of phosphoric acid with a large and interesting group of bodies, viz. the organic alkaloids. It is curious that this class of salts has not been hitherto examined; indeed the composition of scarcely any phosphate of an organic base has been satisfactorily ascertained.

It was a very interesting question, whether these bases, which with monobasic acids comport themselves exactly the same as mineral oxides, were capable of combining with polybasic acids in the same remarkable proportions. In the absence of experiments, the only points which were known from whence we might, by way of analogy, have inferred any similarity in these compounds with the inorganic phosphates, are the salts of ammonia with phosphoric acid; ammonia being as it were the type of all the organic bases. A phosphate of ammonia indeed is known, containing two equivalents of the volatile alkali; but it still remained to be decided whether any true organic alkaloid unites in the proportions of two or more equivalents with one equivalent of phosphoric acid.

The only analysis of a phosphate with an organic alkali is published by Regnault†. This chemist determined the carbon and hydrogen in phosphate of strychnine. Regnault considered the salt which he analysed as a compound of 1 equiv. of phosphoric acid, 1 equiv. of strychnine and water,

$$HO, C_{43} H_{23} N_2 O_4, PO_5.$$

However, Regnault's formula of strychnine has been corrected by Professor Liebig‡, who showed that this base contains one equivalent of carbon more, *i. e.*

$$C_{44} H_{23} N_2 O_4;$$

* Phil. Trans. of Royal Society of London, part 2. 1833. Researches on the Arseniates, Phosphates and Modifications of Phosphoric Acid, by Thos. Graham, Esq., M.A., F.R.S.E., Professor of Chemistry in the Andersonian University of Glasgow.

† Liebig's *Annalen*, vol. xxvi. p. 37. ‡ Ibid. vol. xxvi. p. 58.

it is therefore evident that the composition of Regnault's phosphate is to be expressed by the formula

$$HO, C_{44} H_{23} N_2 O_4, 2HO, PO_5,$$

as Professor Liebig * already remarks, and, as may be seen from the following comparison of the per-centages corresponding to this formula with his analytical results, which I have calculated with the new atomic weights of carbon :—

| | | | | |
|---|---|---|---|---|
| 44 eqs. | Carbon . . . . . | 3300·00 | 59·23 | 59·85 |
| 26 ... | Hydrogen . . . . . | 325·00 | 5·83 | 5·85 |
| 2 ... | Nitrogen . . . . . | 354·00 | 6·55 | |
| 7 ... | Oxygen . . . . . | 700·00 | 12·66 | |
| 1 ... | Phosphoric acid . . . | 892·28 | 15·73 | |
| 1 ... | Phosphate of strychnine | 5571·28 | 100·00 | |

It is evident from these numbers that the phosphate of strychnine analysed by Regnault is a common phosphate, corresponding to the phosphate of soda with 1 equiv. of fixed base.

Besides this, Dr. A. T. Thomson † relates an analysis of phosphate of morphine by Dr. Gilbert, from which however no conclusion relative to the composition of this salt can be deduced, the analysis being incomplete.

It being a matter of indifference whether the base which I took for experiment was a natural alkaloid or one prepared artificially in the laboratory, I selected aniline, deeming it especially suited to my purpose, as this base generally forms with acids readily crystallizable compounds.

## I. Compounds of Tribasic Phosphoric Acid with Aniline.

### 1. *Phosphate with 2 equivs. of Aniline and 1 equiv. of Water.*

On adding aniline in excess to a strong solution of tribasic phosphoric acid, the whole instantly solidified to a white crystalline mass, which was drained, pressed, dissolved in a large quantity of boiling dilute alcohol, and filtered through a warm funnel; on cooling, the whole became a mass of crystals; after pressing these between folds of bibulous paper, I finally dried them on a warm porous tile.

When dry, this salt appears as beautiful flesh-coloured nacreous plates, which might be readily taken for thionurate of ammonia, quite inodorous, slightly acid to test paper. They are very soluble in æther and water, sparingly soluble in cold

* *Handwörterbuch der Chemie*, article 'Organic Bases,' vol. i. p. 70.

† Pharm. Journal, vol. ii. p. 500, 'On the Preparation, Characters, and Composition of the Nitrate, Phosphate, Tartrates and Hydriodate of Morphia,' by Anthony Todd Thomson, M.D., F.L.S.

alcohol, but very soluble in hot, so that upon cooling the whole liquid becomes solid. This salt cannot be dried at 100° C. (212° F.), because at this temperature it gives off aniline, assuming a red colour. It melts at a gentle heat, and upon raising the temperature gives off its aniline and leaves metaphosphoric acid.

*Analysis.*

When burnt with oxide of copper—

I. 0·419 grm. of the substance gave 0·774 grm. of carbonic acid and 0·227 grm. of water.

II. 0·646 grm. of the substance gave 1·183 grm. of carbonic acid and 0·356 grm. of water.

III. 1 grm. neutralized with ammonia and precipitated with nitrate of silver, gave 1·461 grm. of tribasic phosphate of silver.

These numbers correspond with the following per-cents.:—

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . . . | 50·38 | 49·94 | |
| Hydrogen . . . | 6·01 | 6·19 | |
| Phosphoric acid . | ... | ... | 24·86 |

These determinations lead to the following formula,

$$2(HO, C_{12}H_7N)\,HO, PO_5,$$

as is seen by the following:—

| | | | |
|---|---|---|---|
| 24 eqs. | Carbon . . . . | 1800·00 | 50·57 |
| 17 ... | Hydrogen . . . | 212·50 | 5·97 |
| 2 ... | Nitrogen . . . . | 354·10 | 9·97 |
| 3 ... | Oxygen . . . . | 300·00 | 8·42 |
| 1 ... | Phosphoric acid . | 892·28 | 25·07 |
| 1 ... | Phosphate of aniline | 3558·88 | 100·00 |

Therefore the salt corresponds to the common phosphate of soda,

$$2NaO, HO, PO_5,$$

and also to an ammonia salt of the same constitution.

It is anhydrous, like this ammonia salt; but, unlike these salts, possesses, as before remarked, an acid reaction, like all the other salts of aniline, this base being incapable of destroying the properties of an acid.

2. *Phosphate with* 1 *equiv. of Aniline and* 2 *equivs. of Water.*

This compound is obtained by adding tribasic phosphoric acid to the salt mentioned before until it ceases to produce a precipitate with chloride of barium, and concentrating in the water-bath. In the course of a few hours the salt crystallizes in beautiful silky needles; these are to be washed with æther and dried on a warm tile.

When dry the salt is quite white, but by exposure to the

air becomes rose-red; it is very soluble in æther, alcohol, and water; in the latter with decomposition, the common phosphate being produced.

*Analysis.*

When burnt with oxide of copper—

I. 0·456 grm. of the substance gave 0·633 grm. of carbonic acid and 0·223 grm. of water.

II. 0·403 grm. neutralized with ammonia and precipitated with nitrate of silver, gave 0·880 grm. of tribasic phosphate of silver.

These numbers correspond to the following per-cents.:—

| | I. | II. |
|---|---|---|
| Carbon . . . . . | 37·86 | |
| Hydrogen . . . . | 5·44 | |
| Phosphoric acid . . | ... | 37·12 |

These determinations lead to the formula

$$HO, C_{12} H_7 N, 2HO, PO_5,$$

as is seen by the following:—

| | | | | |
|---|---|---|---|---|
| 12 eqs. | Carbon . . . . . | 900·00 | 37·59 | 37·86 |
| 10 ... | Hydrogen . . . . | 125·00 | 5·22 | 5·44 |
| 1 ... | Nitrogen . . . . | 177·05 | 7·39 | |
| 3 ... | Oxygen . . . . | 300·00 | 12·54 | |
| 1 ... | Phosphoric acid . . | 892·28 | 37·26 | 37·12 |
| 1 ... | Phosphate of aniline | 2394·33 | 100·00 | |

This salt corresponds to the biphosphate of soda,

$$NaO, 2HO, PO_5.$$

Mitscherlich has analysed an ammonia compound of the same constitution.

I did not succeed in forming a phosphate in which the three equivalents of water in the hydrate are replaced by three equivalents of aniline. On adding aniline in excess to an alcoholic solution of the common phosphate, the base did not combine, and the common phosphate remained. I also tried to produce it by decomposing the phosphate with three equivalents of soda by oxalate of aniline; aniline however was instantly set free in the form of oily globules, and the common phosphate was produced with oxalate of soda.

I have not been more successful in endeavouring to prepare phosphates, into which aniline enters beside fixed bases. I have tried to obtain a salt corresponding to phosphorus salt,

$$NaO, NH_4O, HO, PO_5,$$

by dissolving aniline in a solution of phosphate of soda with one equivalent of fixed base. The crystals, however, which

were formed did not contain soda, and were similar in appearance to the salt first-described. Similar results were obtained by neutralizing the acid phosphate of aniline with carbonate of soda. The salt produced did likewise not contain soda, the common phosphate appearing to be produced.

### II. Pyrophosphate of Aniline.

There are two pyrophosphates of aniline, acid and neutral, which are always formed together when aniline is added in excess to pyrophosphoric acid. The precipitate produced by addition of aniline to pyrophosphoric acid is gelatinous, and becomes quite hard when exposed to the air.

Several combustions showed me that the compound obtained in this way consists of a mixture of the neutral and the acid pyrophosphate. I have not yet been able to obtain the neutral salt in a state of purity, but I found that by keeping the pyrophosphoric acid in great excess, the acid salt may be procured. The best way of forming it is to add aniline to rather concentrated pyrophosphoric acid (obtained by decomposing pyrophosphate of lead by hydrosulphuric acid), when the acid salt is precipitated along with the neutral compound; the mixture is then to be heated until the whole is dissolved, an excess of acid added, and the solution evaporated in the water-bath; upon cooling, the whole solidifies to a mass of beautiful white needles, which are to be pressed in bibulous paper, washed with æther, and finally dried *in vacuo*. This salt appears as white silky needles, very similar to the common basic sulphate of quinine; they are very acid, soluble in water, and almost insoluble in alcohol and æther; the crystals and their aqueous solution, like all other aniline salts, become red when exposed to the air.

#### *Analysis.*

When burnt with oxide of copper—

I. 0·223 grm. of the substance gave 0·333 grm. of carbonic acid and 0·117 grm. of water.

II. 0·269 grm. of the substance gave 0·389 grm. of carbonic acid and 0·132 grm. of water.

III. 0·350 grm. of substance, neutralized by ammonia and precipitated by nitrate of silver, gave 0·578 grm. of pyrophosphate of silver.

These numbers correspond to the following per-cents.:—

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . . | 39·00 | 39·43 | |
| Hydrogen . . | 5·68 | 5·45 | |
| Phosphoric acid | ... | ... | 38·85 |

which lead to the formula

$$HO, C_{12}H_7N, HO, PO_5,$$

as is seen by the following:—

| | | | | |
|---|---|---|---|---|
| 12 eqs. | Carbon . . . . . | 900·00 | 39·44 | 39·22 |
| 9 ... | Hydrogen . . . . . | 112·50 | 4·93 | 5·56 |
| 1 ... | Nitrogen . . . . . | 177·01 | 7·75 | |
| 2 ... | Oxygen . . . . . | 200·00 | 8·77 | |
| 1 ... | Phosphoric acid . . . | 892·28 | 39·11 | 38·85 |
| 1 ... | Pyrophosphate of aniline | 2281·79 | 100·00 | |

This salt corresponds to the acid pyrophosphate of soda,

$$NaO, HO, PO_5,$$

analysed by Professor Graham.

An analogous salt of ammonia is not known, pyrophosphate of ammonia existing only in solution, which, according to Graham's experiments, yields on evaporation crystals of the common phosphate of ammonia, with 2 equivalents of the volatile alkali and 1 equivalent of water.

### III. Metaphosphate of Aniline.

I obtained this salt by adding a great excess of aniline to a very strong solution of metaphosphoric acid (glacial acid perfectly pure), or by adding metaphosphoric acid to a solution of aniline in alcohol or æther; in both cases the salt precipitates as a gelatinous white mass; this is to be placed on a filter and well-washed with æther, until the excess of aniline is removed and no smell of this body perceived, pressed and dried over sulphuric acid *in vacuo*.

When dry the salt appears as an amorphous white mass, which changes rose-red in the air, becoming glutinous. It is acid to litmus paper, soluble in water, and almost insoluble in alcohol and æther.

Its solution dissolves metaphosphate of silver, which property belongs also to metaphosphate of soda; upon boiling, it changes red, and partly reduces the silver salt. When an aqueous solution is boiled for a long time it is transformed into common phosphate of aniline.

#### *Analysis.*

When burnt with oxide of copper—

I. 0·664 grm. of the substance gave 0·976 grm. of carbonic acid and 0·264 grm. of water.

II. 0·994 grm. of the substance, precipitated by acetate of

lead, and the precipitate treated with sulphuric acid, gave 2·617 grms. of sulphate of lead.

III. I also determined the acid by precipitating with acetate of lead in great excess and boiling for a long time; the metaphosphate of lead is completely changed into the tribasic salt. This is a very advantageous method of determining metaphosphoric acid. 0·5785 grm. of the substance gave 1·3485 grm. of tribasic phosphate of lead.

These numbers correspond to the following per cents.:—

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . . . . | 41·33 | | |
| Hydrogen . . . . | 4·55 | | |
| Phosphoric acid . . | ... | 41·24 | 40·98 |

These analyses lead to the formula

$$HO, C_{12}H_7N, PO_5,$$

as is seen by the following:—

| | | | | |
|---|---|---|---|---|
| 12 eqs. | Carbon . . . . . | 900·00 | 41·48 | 41·33 |
| 8 ... | Hydrogen . . . . . | 100·00 | 4·62 | 4·55 |
| 1 ... | Nitrogen . . . . . | 177·01 | 8·11 | |
| 1 ... | Oxygen . . . . . | 100·00 | 4·62 | |
| 1 ... | Phosphoric acid . . . | 892·28 | 41·17 | 41·11 |
| 1 ... | Metaphosphate of aniline | 2169·29 | 100·00 | |

This salt is analogous to Prof. Graham's metaphosphate of soda,

$$NaO, PO_5,$$

which, according to the experiments of this chemist, likewise becomes viscid on evaporation, and never presents the slightest trace of crystallization.

The corresponding metaphosphate of ammonia is only known in solution. On evaporation this salt assimilates 1 equivalent of water, passing into the common phosphate with 1 equivalent of ammonia and 2 equivalents of water.

The experiments which I have described prove that there exist the following series of phosphates of aniline:—

| | |
|---|---|
| Phosphates . . . | $\begin{cases} 2(HO, C_{12}H_7N)\ HO, PO_5. \\ HO, C_{12}H_7N, 2HO, PO_5. \end{cases}$ |
| Pyrophosphate . . | $HO, C_{12}H_7N, HO, PO_5.$ |
| Metaphosphate . . | $HO, C_{12}H_7N, PO_5.$ |

This series embraces compounds corresponding to all the combinations of soda with phosphoric acid, except the phosphate with 3 equivalents of soda, and the pyrophosphate with 2 equivalents of fixed base.

The aniline salt, corresponding to the latter, however exists, but could as yet not be obtained in a state of purity.

All the compounds of aniline with phosphoric acid are anhydrous, like the other salts of this base which have been examined by Professor Hofmann. In this respect they differ from the corresponding soda salts, which nearly all contain a larger or smaller amount of water of crystallization. The two ammonia salts of phosphoric acid which we know, are however likewise anhydrous.

From the results of the preceding investigation we may conclude that the organic bases comport themselves also with polybasic acids like mineral oxides. I intend, however, to analyse the phosphates of some other organic alkaloids, particularly of those which occur in nature, and are frequently employed in medicine.

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## CLXXIV. *On a Common Origin of the Acids* $(CH)_n O_4$ *with a Boiling-point under* 300° *Centigrade.* *By* Dr. Joseph Redtenbacher. (*Translated by* E. F. Teschemacher.)

UNDER this head I include not merely the volatile acids of butter, but also acetic acid, metacetonic acid, valerianic acid, &c.; and, in short, all those acids, according to the above formula, beginning at $n = 4$ to $n = 20$, and including all the intervening members whose values are even numbers of $n$. These are acetic acid, metacetonic acid, butyric acid, valerianic acid, caproic acid, œnanthylic acid, caprylic acid, pelargonic acid (a new acid, $n = 18$), and capric acid.

By former examinations, it is known that they occur and are formed under the most varying circumstances. They are found partly in plants and in animals, in small quantities, as mixtures of solid and fluid fats; their more immediate origin in these cases has not yet been clearly shown. They may be produced from bodies resembling aldehyd, $(CH)_n O^2$, by simply withdrawing the oxygen. The similar theoretical origin of acetic acid, metacetonic, butyric, valerianic and œnanthylic acids has been already proved. That the same has not been accomplished with capric, caprylic and pelargonic acids, is owing to the want of a sufficient quantity for examination. It is not probable that the origin would be found in the organism of the corresponding aldehydes. The different aldehydes by decomposition have been heretofore represented by complex atoms; they have been produced from organic bodies, but not found in them, although the possibility cannot be denied that they may be formed by organic bodies. Another

mode of origin has been made known by Pelouze, namely the production of butyric acid by the decomposition of the hydrate of carbon, of decayed cheese, and of similar bodies; and the production of butyric acid has been detected by Marchand in sour krout and in cucumber-water; and also by Wurz in tainted meat.

Iljenko and Laskowsky, in Liebig's laboratory, have found a considerable quantity of valerianic acid in half-decayed cheese. Cheese which consists of the ingredients of the milk contains only fat and casein; the valerianic acid could only be formed out of these two ingredients. Fresh butter contains no valerianic acid; Liebig has however obtained by the action of caustic alkali on cheese valerianic and butyric acid. But these last two modes cannot be the ordinary way in which these acids exist in organic bodies. It is not especially to be referred to putrefaction or to cheese.

It is probable that nature follows a more general course in producing so great a variety of the easily volatile fatty acids. They are combined with the base lipyloxide, the constant companion of all the fixed and volatile fatty bodies of the vegetable and animal kingdom. The different fatty bodies may be submitted to the same process by which the volatile acids are separated from butter, but in every case a very small quantity of these acids is found.

It is very possible that they proceed either from the fixed acids or from the oily acids of the fat.

The solid acids, stearic, margaric, palmitic, cocinic, myristic, contain carbon and hydrogen in the same proportions; they may merely combine with oxygen in order to be converted, in several equivalents, into acids volatile under 300° Centig., $(CH)_n O_4$.

But these solid acids are in themselves permanent, and do not undergo change by exposure to the air; on the contrary, oleic acid is by the action of the oxygen of the atmosphere, and also by other oxidizable agents, a body subject to changes. According to the formula $C_{36} H_{34} O_4$ of Gottlieb, two atoms of carbon must be given off in order that it may be converted into the acid $(CH)_n O_4$.

Laurent and Bromeis having examined the oxidizing action of nitric acid on the oily acids, the one considered he had found in them œnanthic acid, the other that he had found butyric acid. Tilley, by the action of nitric acid on castor oil, also produced an acid of this class; and still later, Gottlieb, by dry distillation, which is partly an oxidizing process, obtained capric and caprylic acids from oleic acid.

The foregoing considerations have induced me to study the

oxidizable products arising from the action of nitric acid upon oleic acid, but not with the view of repeating or controlling the experiments of Laurent and Bromeis: I have not occupied myself with the products which these two chemists have obtained, but only examined the volatile substances given off on oxidation by the action of nitric acid; I have discovered the before-mentioned series of acids volatile under 300° Centigrade. The oleic acid which served for my experiments was obtained from the stearine factory of this place; it is exclusively obtained from the fat of oxen. It contained some tallow and margaric acid, which did not essentially interfere with the following experiments. When pure stearine is acted upon by soda, and the solution very much concentrated, the decomposition, which is subsequently effected by an acid, gives off the smell of butyric acid; the separated oleic acid melts under 70° C., so that there remains no doubt that even the fixed acids by oxidation give off acids volatile at 300° C., $(CH)_n O_4$.

I made use of a very spacious tubulated retort to effect the oxidation of about 10 gallons contents, the neck of which was furnished with a cooling apparatus. 5 lbs. of the strongest brown fuming acid were poured in, and a funnel provided, whose lower opening dipped into the nitric acid. The acid was slightly warmed, and the oil carefully introduced in small portions at a time. Upon each addition of oil a violent action took place; it was necessary to wait until the previous action had subsided before any fresh addition of oil was made. The thick brown fumes condensed partly in the water of the receiver through which it passed. Sometimes drops of oil appeared on it, and the passing nitrous gas smelt strongly of volatile fatty acids. After 2 or 3 lbs. of oleic acid had been added, the further oxidation was assisted by heat. When, after long heating, a quantity of oil remains on the surface, a fresh portion of nitric acid may be added, using the same precautions as when the oil was added. In this way I have digested 3 or 4 lbs. of oleic acid for several days with nitric acid. At last I obtained, by the addition of water and redistillation, all the volatile products contained in the retort. The products of the distillation were partly saturated with potash and subjected to a fresh distillation. In the retort there remained nitrate of potash; the colourless distilled product had floating upon the surface strata of volatile fatty acids, and the easily soluble acids were dissolved in the water. The oily portion was drawn off by a siphon and neutralized by baryta water, the different acids separated by crystallization. It contained all the acids, from the valerianic to the capric. The

solution of the easily soluble acids was neutralized by carbonate of soda and evaporated to a syrup. Acetate of soda first crystallized out. The mother-liquor was decomposed by sulphuric acid, the floating oily stratum drawn off, and the acetic, metacetonic and butyric acids were partly separated from one another by their boiling-points; the acetic acid and the metacetonic were determined by a silver salt, and the butyric acid by a barytic salt. It may be conceived that the separation of these nine acids, possessing such similar properties, was effected with much difficulty. It is already troublesome to separate the four volatile acids of butter by means of the crystallization of the barytic salts; nearly one-third of the barytic salts remain as an inseparable mixture. The volatile acids of butter differ in the amount of the factor $n$, but not more than 4, while the series with which I was occupied differed only 2. The similarity of the properties of the barytic salt, or, what is the same thing, the difficulty of their separation, was therefore twice as great. I had therefore a large quantity of the mixed barytic salts which was unfit for examination; it would have been impossible to exhibit separately all the acids unless I had had 4 oz. of the mixed volatile acids.

Before I made use of the barytic salts I tried the separation of the hydrated acids by means of their boiling-point. According to recent experiments of Kopp and Fehling, it appears that the hydrated acids $(CH_n)\,O_4$ increase in their boiling-point about 20° C. when the factor $n$ is augmented by 2. But when I undertook the distillation, the thermometer rose so regularly from degree to degree that I soon discovered the futility of this mode of separation. A portion of the acid hydrates which came over at the boiling-points of butyric acid, 164° C. and about 4° lower, were converted into silver salts; they proved to be upon examination a mixture of three acids, —the butyric acid, the next lower, the metacetonic, and the next higher, the valerianic acid. Therefore, as a complete separation could not be effected by distillation of the hydrated acids, I did not attempt the separation by means of the ethyl compounds, which would in all probability have acted in the same manner.

For the less volatile acids, from valerianic to capric acids, I had recourse to the barytic salts. By gentle evaporation and crystallization I obtained a series of about twenty crystallizations, and by means of an examination according to their known atomic weights, I was enabled to refer the separate crystallization to their different acids, and by subsequent recrystallization of the different portions to separate them

perfectly from one another, taking only the middle portion of each.

I had originally intended only to undertake the examination of the volatile acids of butter, but the form of the barytic salts led me to the expectation and to the discovery of the intervening acids. If the crystallization of the four volatile acids of butter be compared, it is found that they all crystallize in forms which are only of different sizes and differently grouped. The prisms of caprate of baryta are microscopical, and appear like fine powder. Those of caprylate of baryta are united in small grains; the groups of the caproate of baryta are much larger; and the baryta salts of the butyric acid crystallize in groups as large as hazel-nuts. The other three intervening acids, whose factor $n$ is not divisible by 4 but by 2, crystallize in scaly clusters of a pearly lustre, as is already known to be the case with valerianic acid and œnanthylic acid.

I will now give the analytical results of the series, beginning with the lowest. It is to be observed, that in the analysis of bodies presenting so many difficulties, the results cannot be expected to agree perfectly with the theory.

1. *Acetic Acid.*—The silver salts were formed from crystallized acetate of soda; it gave 69·19 per cent. of oxide of silver; theory requires 69·46 per cent.

2. *Metacetonic Acid.*—As before mentioned, the mother-liquor, from which the acetate of soda was crystallized, was decomposed by sulphuric acid. An oily stratum was produced, which was distilled over. It began to boil at 110° C.; what came over from 120° to 140° was neutralized by ammonia and precipitated with nitrate of silver, then boiled until completely dissolved. On cooling, the silver salt was deposited in small hard grains and druses, which blackened at 100° C., and at a higher temperature fused and decomposed. It had all the other properties of metacetonate of silver. 0·242 grm. dried in vacuum gave 0·144 grm. silver; and further, 0·203 grm. gave 0·1525 grm. carbonic acid and 0·057 grm. water.

| | | Theory. | Experiment. |
|---|---|---|---|
| 6 eqs. | Carbonic acid . . . . | 450·0 | 19·89 | 20·49 |
| 5 ... | Hydrogen . . . . . | 62·5 | 2·76 | 3·12 |
| 3 ... | Oxygen . . . . . | 300·0 | 13·26 | 12·47 |
| 1 ... | Oxide of silver . . . | 1450·0 | 64·09 | 63·92 |
| 1 ... | of Metacetonate of silver | 2262·5 | 100·00 | 100·00 |

3. *Butyric Acid.*—The oily acid just mentioned under metacetonic acid as passing over at 140° to 164° C. was saturated with baryta and crystallized. The first two crystal-

lizations still contained valerianic acid; the third and fourth crystallizations had all the properties of butyric acid, and were again crystallized; upon analysis it gave the following result. This, as well as all the following analyses, was made with chromate of lead.

0·415 grm. butyrate of baryta gave 0·261 grm. carbonate of baryta; 0·4697 grm. of the same salt gave 0·5265 grm. carbonic acid and 0·1955 grm. water.

| | | Calculated. | | Found. |
|---|---|---|---|---|
| 8 eqs. | Carbonic acid . . | 600·0 | 30·86 | 30·57 |
| 7 ... | Hydrogen . . . | 87·5 | 4·50 | 4·62 |
| 3 ... | Oxygen . . . . | 300·0 | 15·43 | 15·95 |
| 1 ... | Baryta . . . . | 956·9 | 49·21 | 48·86 |
| 1 ... | Butyrate of barytes | 1944·4 | 100·00 | 100·00 |

As already stated, the oily stratum which floated on the liquid in the receiver, and which contained the less soluble acids, was saturated with caustic baryta, and a series of crystallizations of the baryta salts thus produced.

4. *Valerianic Acid.*—The soluble salts below crystallized in clusters of large plates, with the known properties of valerianate of barytes.

0·268 grm. valerianate of barytes gave 0·154 grm. carbonate of barytes; 0·394 grm. gave 0·506 grm. carbonic acid and 0·1935 grm. water.

| | | Calculated. | | Found. |
|---|---|---|---|---|
| 10 eqs. | Carbonic acid . . . | 750·0 | 35·38 | 35·03 |
| 9 ... | Hydrogen . . . . | 112·5 | 5·31 | 5·46 |
| 3 ... | Oxygen . . . . | 300·0 | 14·15 | 14·87 |
| 1 ... | Baryta . . . . . | 956·9 | 45·16 | 44·64 |
| 1 ... | Valerianate of baryta | 2119·4 | 100·00 | 100·00 |

5. *Caproic Acid.*—The foregoing second and third crystallizations of the valerianate of baryta appeared in small semiglobular druses, which were made up of small prismatic crystals. These were now recrystallized, and had then all the appearance and properties of caproate of barytes.

0·282 grm. gave 0·149 carbonate of barytes; 0·5085 grm. gave 0·7255 carbonic acid and 0·270 grm. water.

| | | Calculated. | | Found. |
|---|---|---|---|---|
| 12 eqs. | Carbonic acid . . . | 900·0 | 39·22 | 38·92 |
| 11 ... | Hydrogen . . . . | 137·5 | 5·99 | 5·90 |
| 3 ... | Oxygen . . . . . | 300·0 | 13·08 | 14·14 |
| 1 ... | Baryta . . . . . | 956·6 | 41·71 | 41·04 |
| 1 ... | Caproate of barytes . | 2294·4 | 100·00 | 100·00 |

6. *Œnanthylic Acid.*—Between the crystallization of ca-

proate of baryta and the foregoing fine granular crystals of caprylate of baryta, there appeared crystals in large plates, with a mother-of-pearl lustre, which recrystallized several times in the same form. It appeared from analogy that it could only contain an acid whose composition was between the caproic and caprylic acids, or it rather was presumed to be with certainty the œnanthylic acid discovered by Tilley. The quantity of the salt obtained was very small, only a few grammes, nevertheless it was necessary to recrystallize it in order to take only the middle portions. I obtained only about 400 milligrammes of the pure salt for examination, of which a part was used for qualitative analysis. The properties however agreed in every respect with the œnanthylate of baryta of Tilley. There remained only sufficient for the determination of the atomic weight of the salt.

0·3273 grm. œnanthylate of baryta gave 0·162 grm. carbonate of baryta; this gave œnanthylate of baryta :—

| | Calculated. | Found. |
|---|---|---|
| Atomic weight . . . . . | 2469 | 2489 |
| Anhydrous acid . . . . . | 1413 | 1413 |
| In 100 parts,—Baryta . . | 38·73 | 38·45 |

7. *Caprylic Acid.*—The before-mentioned very small fine granular crystals from œnanthylate of baryta were decomposed by sulphuric acid; they gave out the odour of sweat, and formed the known properties of caprylic acid. I have obtained crystals of caprylate of baryta in other forms. I left a cold saturated solution of this salt for eight months in a glass vessel covered with blotting-paper to spontaneous evaporation. During this time the solution had evaporated to three-quarters of its former bulk, and at the bottom were deposited prismatic crystals, above one-quarter of an inch in length, very hard, with a waxy lustre. The atomic weight showed me that they were pure caprylate of baryta.

Of the above fine granular crystals, 0·493 grm. gave 0·229 grm. carbonate of baryta; 0·3265 grm. gave 0·545 grm. carbonic acid and 0·212 grm. water.

| | | Calculated. | | Found. |
|---|---|---|---|---|
| 16 eqs. | Carbon . . . . | 1200·0 | 45·38 | 45·51 |
| 15 ... | Hydrogen . . . | 187·5 | 7·09 | 7·22 |
| 3 ... | Oxygen . . . . | 300·0 | 11·35 | 11·19 |
| 7 ... | Baryta . . . . | 956·9 | 36·18 | 36·08 |
| 1 ... | Caprylate of baryta | 2644·4 | 100·00 | 100·00 |

8. *Pelargonic Acid.*—Between capric and caprylic acids no

other acid was previously known to exist. When the crystallizations of the mixed barytic salts were made, crystals of caprylate of baryta formed on the powder of the caprate. I have already mentioned in my work upon the products of the oxidation of choloidic acid, that a barytic salt in large plates, with a mother-of-pearl lustre, was formed between the caprate and caprylate of baryta, which, from its variable composition, I considered as a mixture of the two salts. But during my proposed examination I obtained between caprate and caprylate of baryta, in the third and fourth crystallizations, a salt of barytes in large plates, which remained the same after repeated crystallization; they were purified in the same manner as the other salts, by taking only the middle portions of the crystals. I consider I am not hasty, even with so imperfect a knowledge, to admit the existence of a new acid, and which analysis confirms to contain the factor $n=18$. I name it, upon grounds which I shall subsequently state, pelargonic acid.

Pelargonate of baryta crystallizes, as I have already stated, similarly to valerianate and œnanthylate of baryta, but is much less soluble in water and in alcohol; it is considerably more soluble than caprate of baryta, and, as it crystallizes out before caprylate of baryta, it is therefore less soluble than this latter salt. It has properties between these two salts. In its other properties it naturally corresponds with the barytic salts of all the volatile fatty acids. It gave out at 100° C. a very small quantity of water, so that its crystals are anhydrous.

0·3395 grm. gave 0·148 grm. carbonate of baryta; 0·316 grm. gave 0·5485 grm. carbonic acid and 0·212 grm. water.

| | | Calculated. | | Found. |
|---|---|---|---|---|
| 18 eqs. | Carbon . . . . . | 1350·0 | 47·88 | 47·34 |
| 17 ... | Hydrogen . . . . | 212·5 | 7·54 | 7·46 |
| 3 ... | Oxygen . . . . . | 300·0 | 10·64 | 11·34 |
| 1 ... | Baryta . . . . . | 946·9 | 33·94 | 33·86 |
| 1 ... | Pelargonate of baryta | 2809·4 | 100·00 | 100·00 |

The mother-liquor from which the above barytic salts were crystallized, and which doubtless still contained caprylic acid, as a trial of it proved, was precipitated by nitrate of silver. A white curdy precipitate fell, which was with difficulty soluble in hot water. The precipitate was dried at 100° C.

0·198 grm. pelargonate of silver gave 0·0815 grm. silver; 0·3845 grm. of the salt gave 0·5635 grm. carbonic acid and 0·219 water.

| | | Calculated. | | Found. | Pless*. |
|---|---|---|---|---|---|
| 18 eqs. | Carbon . . . . . | 1350·0 | 40·75 | 39·98 | 40·88 |
| 17 ... | Hydrogen . . . . | 212·5 | 6·42 | 6·33 | 6·46 |
| 3 ... | Oxygen . . . . . | 300·0 | 9·06 | 9·48 | 8·89 |
| 1 ... | Oxide of silver . . | 1450·0 | 43·77 | 44·21 | 43·77 |
| 1 ... | Pelargonate of silver | 3312·5 | 100·00 | 100·00 | 100·00 |

A small quantity of caprylic acid contained in it decreased the carbon and the water, but increased the quantity of oxide of silver.

9. *Capric Acid.*—Of all the foregoing acids, the action of nitric acid upon the oily acids produces the smallest quantity of this acid, it being the strongest combination, and containing the smallest quantity of oxygen; and also from possessing the highest boiling-points, during the distillation with the nitric acid and water, the smallest quantity is distilled over. Having dissolved all the barytic salt in water, the first crystallization had all the appearance of caprate of baryta. The atomic weight was considerably higher than that of the pelargonate of baryta, but not so high as that of the caprate of baryta. By means of crystallization, redissolving the first-formed crystals and recrystallizing, I at last raised the atomic weight to 2950; but pure caprate of baryta possesses an atomic weight of 2990. Although I had not enough of the substance to submit it to combustion, still there is no doubt that capric acid had been formed. With this is closed the series of these volatile fatty acids, which are obtained by the action of nitric acid upon the oily acids. The largest in quantity formed are the caproic, valerianic and acetic acids; the next in quantity are caprylic, butyric and metacetonic acids; and the least in quantity formed are the capric, pelargonic

* H. Pless undertook some time ago the examination of the volatile ingredients of the plant *Pelargonium roseum*, (so called from the known scent of the rose), but could not complete it for want of sufficient material. He distilled the plant with water; the product had the scent of the plant, and an oil swam at the top. The liquid had a sour reaction. It was neutralized by baryta water, and the neutral, strongly-scented oil was distilled over. The solution evaporated to dryness contained fatty acids. It was boiled in alcohol, and the first product precipitated by nitrate of silver.

0·284 grm. gave 0·1157 grm. silver; another portion of 0·354 grm. gave 0·5305 grm. carbonic acid and 0·2058 grm. water.

The calculation of this analysis is given above under the head of Pless. This is the reason, for want of a better, that I gave it the name pelargonic acid. Respecting the properties of the hydrates of pelargonic acid, I have little to notice, as the quantity of it I possessed was too small. It is an oily, greasy acid, slightly soluble in water, but easily soluble in alcohol and æther. With regard to its other properties, as far as experiments lead, it may be considered to hold a middle place in the hydrates between the capric and caprylic acids.

and œnanthylic acids. Before I make any further observations in connection with these acids, I will refer to a non-volatile body, which is also obtained by the oxidation of the oily acids, and which appears as a middle member that first originates from oily acids and then changes, on the one hand, into suberic and pimelic acids, and, on the other, by the presence of water into the volatile fatty acids. If the oxidation is not carried so far that the last trace of the fatty stratum in the retort does not disappear, there floats on the surface of the water on cooling an oily stratum of an unguent consistency, which, after washing with water, possesses a strong odour of sweat. This unctuous body is heavier than water, easily soluble in alcohol and æther, but not capable of being distilled over. If heated to above 100° C., a kind of combustion takes place of its elements, giving out an odour of cinnamon and nitrous acid; volatile fatty acids distil over, and the remainder becomes quite black and tough; suberic acid may be detected in it; when acted upon by an alkali it is dissolved with a blood-red colour, and can be again separated unchanged by an acid. When boiled with water in a retort it undergoes decomposition, and volatile fatty acids distil over into the receiver; suberic and pimelic acid remain dissolved in the water in the retort, and the first acid may be crystallized out. These bodies therefore appear to consist of that portion of the atom of the oily acids combined with nitrous acid which produce suberic and pimelic acids, $(CH)_n O_4$.

As it was not possible to obtain it free from mixture, I did not submit it to any further examination. The common origin of the volatile fatty acids from the oily acids clearly accounts for the wide-spread occurrence of these with the oily acids in all fat.

As before stated, I have for many years examined, partly myself and partly by means of others, the volatile acids contained in animal fat, namely, the fat of fowls, of geese, snakes, badgers, hares, particularly human fat, and several others, and in every one, without exception, I have discovered small portions of volatile fatty acids. The most common appear to be the caprylic, caproic and valerianic acids.

Human fat, which M. Lerch very carefully examined, and in large quantities, gave, with the known margaric and oleic acids, a considerable quantity of volatile fatty acids besides caprylic acid, so that the barytic salt of the latter could be clearly established. As before stated, the weakened odour of caprylic acid brings to my mind the ordinary odour of the perspiration of a healthy man; and it is therefore probable

that this acid passes off with the perspiration of the body after strong exercise and heating.

According to the knowledge we possess concerning the fat of plants and of animals, the combinations of the volatile and non-volatile acids are with lipyloxide. A person the least accustomed can with ease distinguish by their smell the difference between the fat of oxen, of pigs, or of fowls, particularly when the fat is heated to the melting-point, but still the composition of them all is the same. If the fat is washed and the acids separated, it is no longer possible to distinguish between them (butter is an exception). During the washing the substances disappear which are characteristic of the different fats; they appear to have volatilized or to be decomposed. The substance to which the peculiar smell of the fat is due has not yet been isolated. It is possible that it is the corresponding lipyloxide combination of the volatile fatty acids.

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## CLXXV. *On the Formation of Nitric Acid in Eudiometric Combustions of Gases mixed with Nitrogen.* *By* Dr. H. Kolbe.

IN an analysis of mixed gases, which contained 90 parts of light carburetted hydrogen and 10 parts of nitrogen, I have often found, that by the combustion in the eudiometer more oxygen disappeared than in accordance with the calculation ought to have disappeared. The explosion caused always such an elevation of temperature, that the mercury sublimed and covered the inside of the eudiometer with a thin, gray, metallic film. After the caustic potash-ball was introduced into the eudiometer for the purpose of absorbing the carbonic acid formed, and the residual volume of gas dried, the diaphanous film of mercury was seen to be covered by innumerable little white crystals, the behaviour of which with water, muriatic acid and caustic potash, showed clearly that they contained protoxide of mercury for their basis.

If these crystals consist of nitrate of protoxide of mercury, as the well-known experiments by Cavendish on the formation of nitric acid render probable, then the before-mentioned diminution of the volume is easily understood.

Therefore, trying at first whether this error was occasioned only by the presence of nitrogen, I mixed a certain volume of pure hydrogen with an excess of oxygen in an eudiometer*

* In all these experiments I used an eudiometer which was furnished with a correctly graduated millimetre-scale etched upon the glass, and exactly graduated, on which by employing a mirror it was easy to determine

over mercury, and after having exploded the mixture, I observed the diminution of the volume of gas.

[The volumes found by observation in this and the following examples were saturated with the vapour of water.]

*Experiment* I.

| | Vol. obs. | Temp. | Barom. | Height of mercury in tube over that in trough. | Corr. vol. |
|---|---|---|---|---|---|
| Hydrogen . . . . | 78·8 | 11·2°C. | 764·7mm | 366·0mm | 29·4 |
| After admission of O. | 137·6 | 11·0 | ... | 305·2 | 59·5 |
| After combustion . | 45·6 | 11·0 | ... | 400·3 | 15·5 |

*Experiment* II.

| | | | | | |
|---|---|---|---|---|---|
| Hydrogen . . . . | 145·5 | 12·0°C. | 764·7mm | 297·9mm | 63·6 |
| After admission of O. | 281·4 | 11·5 | ... | 162·1 | 159·9 |
| After combustion . | 146·5 | 11·3 | ... | 296·5 | 64·4 |

When we calculate the quantity of the consumed hydrogen from the whole volume of gas which has disappeared by combustion, we find numbers which correspond exactly with the hydrogen used.

| | I. | II. |
|---|---|---|
| Hydrogen used . . . . | 29·4 | 63·6 |
| ... calculated . . | 29·4 | 63·6 |

By this similarity of the results as found and calculated, it is evident that the mercury cannot become oxidized when pure hydrogen is burnt with an excess of oxygen. Mercury sublimed also in this case; but no trace of the crystals spoken of could be seen, even when the residual gas was dried.

Varying the experiments, I mixed with a similar explosive mixture a small portion of atmospheric air (which is calculated to contain in 100 vols. 20·9 vols. of oxygen); I obtained the following results, very different from the former:—

*Experiment* III.

| | Vol. obs. | Temp. | Barom. | Height of mercury in tube over that in trough. | Corr. vol. |
|---|---|---|---|---|---|
| Atmospheric air . . | 76·8 | 8·8°C. | 767·9mm | 367·2mm | 29·2 |
| After admission of H. | 246·0 | 8·8 | 768·2 | 197·0 | 134·1 |
| After admission of O. | 402·9 | 9·5 | 768·3 | 45·8 | 277·8 |
| After combustion . | 225·1 | 9·6 | 768·4 | 218·2 | 117·8 |

the tenth part of a millimetre. I also took care to observe all the precautions, by which Bunsen has excluded everything that can occasion an error. The mercury was previously purified by digesting for some days with nitric acid, and had all the properties of the pure metal.

*Experiment* IV.

| | Vol. obs. | Temp. | Barom. | Height of mercury in tube over that in trough. | Corr. vol. |
|---|---|---|---|---|---|
| Atmospheric air . . | 79·2 | 8·4°C. | 773·0mm | 364·2mm | 30·7 |
| After admission of H. | 250·4 | 8·5 | 773·7 | 192·4 | 139·1 |
| After admission of O. | 391·7 | 8·5 | 773·7 | 55·8 | 269·4 |
| After combustion . | 200·3 | 8·6 | 773·4 | 241·9 | 101·5 |

| | III. | IV. |
|---|---|---|
| Hydrogen used . . . | 104·9 | 108·4 |
| ... calculated . | 106·8 | 111·9 |

According to these experiments, it appears impossible to determine accurately in the usual way, by combustion with oxygen, the quantity of a combustible gas when nitrogen is present, on account of the simultaneous oxidation of the nitrogen producing from 2 to 3 per cent. more hydrogen, as shown by the last two experiments, and which under more unfavourable circumstances is liable to be still increased. Notwithstanding the dilution with atmospheric air, the elevation of the temperature on combustion was so great, that the inner surface of the eudiometer was covered with sublimed mercury, upon which was deposited a number of microscopic crystals; they made their appearance as soon as the remaining gas was dried by means of chloride of calcium.

One of the conditions which in the above case appears to be absolutely necessary for the formation of nitric acid, is the great elevation of temperature of the gas during combustion. The lowering the temperature to a certain point is sufficient entirely to prevent the oxidation of the nitrogen. This is best accomplished by diluting the combustible gas with 1, 2 or 3 volumes of atmospheric air, by which means the accuracy of the analysis is not in the least affected. The following analysis, where hydrogen was deflagrated with twice its volume of atmospheric air mixed with the requisite quantity of oxygen, will justify this assertion, besides which I have been able to confirm it by a series of other experiments.

| | Vol. obs. | Temp. | Barom. | Height of mercury in tube over that in trough. | Corr. vol. |
|---|---|---|---|---|---|
| Atmospheric air . . | 212·3 | 14·2°C. | 756·9mm | 244·8mm | 100·9 |
| After admission of H. | 282·7 | 15·1 | 757·4 | 175·3 | 152·5 |
| After admission of O. | 321·6 | 15·4 | 758·3 | 137·3 | 185·1 |
| After combustion . | 221·7 | 14·7 | 758·5 | 234·0 | 107·7 |

| | Used. | Calculated. |
|---|---|---|
| Hydrogen . . . | 51·6 | 51·6 |

Professor Bunsen has been so kind as to communicate to me the following very interesting series of experiments relating to this subject, proving clearly that the formation of nitric acid is diminished in the combustion of explosive mixtures according to the dilution with atmospheric air. He mixed a constant quantity of atmospheric air with a decreasing quantity of pure explosive gas formed by decomposing water by means of electricity, and obtained the following results on combustion:—

| Vol. | | | | Vol. | | Vol. |
|---|---|---|---|---|---|---|
| 100 atmospheric air gave after combustion with | | | | 259·70 | explosive gas | 86·15 |
| 100 | ... | ... | ... | 226·80 | ... | 88·56 |
| 100 | ... | ... | ... | 84·98 | ... | 99·19 |
| 100 | ... | ... | ... | 63·21 | ... | 99·97 |
| 100 | ... | ... | ... | 48·98 | ... | 99·99 |
| 100 | ... | ... | ... | 40· | ... | 100·10 |
| 100 | ... | ... | ... | 36·39 | ... | 100·36 |
| 100 | ... | ... | ... | 21·20 | ... | 100·79 |

100 air mixed with 11 vols. of explosive gas did not ignite.

By this it is proved that the ignition of combustible gases containing nitrogen must not be attempted at too far a limit from the point at which the mixed gases are combustible. This point may be ascertained with an unknown mixture by previous experiment, as the gas before its separation from the carbonic acid, &c. may be mixed with nearly double its volume of oxygen gas (which quantity is sufficient even if it consisted of pure light carburetted hydrogen), and small portions added by degrees to a known volume of atmospheric air in an eudiometer until ignition by means of the electric spark took place. For example, if it is found that 50 volumes of such a mixture with 100 volumes of atmospheric air will just ignite, then, according to the foregoing experiments, treble the quantity of the former mixture may be ignited without the formation of nitric acid. Therefore, in an eudiometrical analysis, the gas to be examined may be mixed with twice its volume of atmospheric air, besides the requisite quantity of oxygen gas. In this manner it is ascertained whether the gas to be analysed requires still a dilution with atmospheric air.

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## CLXXVI. *On Tribasic Boracic Æther.*

*By* J. E. Bowman, *Esq.*

A FEW months ago M. Ebelmen published an account of two compounds of silicic acid and æther, and announced that by subjecting them to the gradual action of moist air, he

had succeeded in obtaining specimens of hydrated silicic acid perfectly hard and transparent.

This was the first time silica had been obtained artificially in a state at all resembling quartz; and though it is anything but probable that nature ever manufactured her rock-crystal or hydrophane by the action of moist air on silicic æther, I felt interested in the subject, and prepared a quantity of the æther according to Ebelmen's directions, viz. by mixing together liquid chloride of silicon and absolute alcohol. I then placed a little of the æther in some test-tubes, closed them with corks having a small slit cut down the sides, to allow the access of air, and put them, with a small pan of water, under a bell glass.

In the course of a couple of months a thin ring of transparent silica was deposited round the inside of the tubes, an inch or two from the surface of the æther, apparently at the point where the æthereal vapour had come in contact with the moist air. This silica, though hard, is extremely brittle, and will scarcely bear removal from the glass on which it is deposited without injury. It appears destitute of crystalline structure, and is wholly without action on polarized light.

It occurred to me as highly probable, from the analogous properties of silicon and boron, that if chloride of boron were carried into absolute alcohol, a boracic æther would be produced by a decomposition similar to that of the chloride of silicon.

I passed pure and perfectly dry chlorine over an ignited mixture of charcoal and boracic acid, and purified the gas thus formed from the free chlorine with which it was mixed, by passing it through two U-shaped tubes filled with copper turnings. To the last of these I connected two of Liebig's bulb-apparatus charged with absolute alcohol.

As soon as the gas began to fill the first bulb, a heavy liquid was deposited above the surface of the alcohol, through which it sank and gradually mixed, forming a clear solution. The temperature of the liquid rose considerably during the formation of this heavy fluid, and to prevent it getting too hot I immersed the bulbs in cold water.

After some time the liquid in the bulbs became turbid, owing to the formation of minute globules of a new fluid immiscible with the first; this gradually increased considerably in quantity, and at length occupied nearly as much space as the other. This new fluid was considerably lighter than the first, and the globules as they separated rose to the surface, forming a distinct layer, similar to oil floating on the surface of water.

During the formation of this second fluid the temperature

did not sensibly change, though it had risen considerably while the heavy one was forming. The weight of the liquid in the bulbs increased during the operation about 50 per cent.

From the heavy fluid I have been unable to obtain, after repeated distillations, a perfectly homogeneous compound. It appears to consist chiefly of a chlorinated compound, and gives on analysis—

| | |
|---|---|
| 46·29 C<br>11·86 H<br>32·32 O | nearly in the proportion of alcohol; |
| 9·53 Cl | and a trace of boracic acid. |
| 100·00 | |

When first distilled it gave off a large quantity of acid fumes, consisting chiefly of hydrochloric acid and chloride of æthule. Its boiling-point appears to be about 190°, and its specific gravity 0·901. Its smell is aromatic, its taste acid and pungent. It fumes slightly in the air, and is miscible with alcohol and æther. Ammonia decomposes it, with formation of muriate of ammonia, and solution of potash produces chloride of potassium. It is very combustible, reddens litmus, and turns turmeric brown.

Though the two fluids are apparently so completely immiscible, they nevertheless dissolve each other to a certain extent, and retain that small quantity with very considerable force; so that in almost every rectification of the heavy liquid a few drops of the lighter one distilled over.

The lighter liquid has furnished more satisfactory results. When first heated it gave off fumes of hydrochloric acid and chloride of ethule. It retained with considerable tenacity a small portion of the heavy fluid, with which it evidently mixes in small and definite quantity, and then refuses to dissolve any more, as is the case with many other liquids, as water and common æther.

In the fourth distillation I obtained a pure product, having a specific gravity of ·871 and boiling at 250°. It is curious that though this is considerably the lighter of the two fluids, its boiling-point is 60° higher than the other.

I first attempted its analysis with oxide of copper, but found it impossible to obtain constant results. Four analyses with chromate of lead gave,—

| | I. | II. | III. | IV. | Mean. |
|---|---|---|---|---|---|
| C . . | 47·76 | 48·12 | 47·20 | 47·68 | 47·69 |
| H . . | 9·85 | 9·95 | 9·82 | 9·98 | 9·90 |
| $BO_3$ . | 23·81 | 24·94 | 23·43 | 25·01 | 24·29 |
| Chlorine | | (accidental) | | | ·18 |

It is therefore clearly a tribasic æther, the carbon and hydrogen being in the proportions to form æther, and the boracic acid being in slight excess. The calculated results would be,

| | |
|---|---|
| Carbon . . . . . | 49·34 |
| Hydrogen . . . . . | 10·27 |
| Oxygen . . . . . | 16·45 |
| $BO_3$ . . . . . | 23·94 |
| | 100·00 |

The density of the vapour confirms this view of its composition :—

| | |
|---|---|
| Weight of globe filled with air . . | 1550·93 gr. |
| Temperature of air . . . . . | 58° |
| Pressure . . . . . | 30·61 inch. |
| Temperature of bath when sealed . . | 278° |
| Weight of globe full of the vapour . | 1573·14 |
| Weight of air in globe (corrected) . | 8·068 gr. |
| Weight of vapour in globe at 278° . | 30·278 gr. |
| Weight of 100 cubic inches of vapour at 60° and 30 inches . . . . | 164·81 gr. |
| Specific gravity of vapour . . . . | 5·31 |
| Calculated specific gravity of vapour, supposing it to consist of 3 equivalents of æther and 1 of $BO_3$ condensed into 4 oxygen vols. | 5·05 |

From this it appears that it has suffered the same amount of condensation as most of the monobasic æthers, notwithstanding it contains 3 equivalents of æther instead of 1. The theory of its formation from alcohol and chloride of boron is very simple :

$$BCl_3, 3(C_4H_6O_2) = 3HCl + BO_3, 3(C_4H_5O).$$

Tribasic boracic æther is a colourless liquid, with a pungent, slightly aromatic smell and acrid taste. It fumes when exposed to moist air, owing to the decomposition of its vapour, and round the stopper of the bottle containing it, is generally formed a downy deposit of boracic acid.

When a drop of water is added to it, boracic acid is immediately precipitated, which is redissolved when more water is added. A similar decomposition takes place when mixed with solutions of ammonia and potash, borates of those bases being formed. With alcohol and æther it is miscible in all proportions. It burns with a bright green flame, giving off white fumes of $BO_3$, and leaving a residue of the fused acid. The colours of dry litmus and turmeric are not changed by

it, but when moist the first is reddened and the latter becomes brown, owing to the liberation of boracic acid.

I am now engaged in examining the effects of passing some of the volatile metallic chlorides into absolute alcohol; and I am not without hope that I shall be able in this way to form some metallic æthers.

Since writing the above I have seen in the last number of the *Annales de Chimie*, which has just reached us, a notice that M. Ebelmen has also succeeded in forming the tribasic æther I have now described, and has also formed a similar compound with oxide of methyle. Our results appear to be almost identical, excepting that his numbers approach the calculated ones somewhat more closely than my own.

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Nov. 2, 1846.—The President in the Chair.

Presents were announced to the Museum:—from Dr. Hermann Bleibtreu, a Specimen of Coumarin; from Mr. Nicholson, of the Phosphate and Metaphosphate of Aniline; from Mr. Warington, of Nitrate of Soda in fine crystals. To the Library:—from Dr. George Wilson, Essays "On Wollaston's argument, from the limitation of the Atmosphere, as to the finite divisibility of Matter;" "On the applicability of the Electro-magnetic Bell to the trial of experiments on the conduction of Sound, especially in Gases;" "On a simple mode of constructing Skeleton Models to illustrate the systems of Crystallography;" from the Franklin Institute, the consecutive Numbers of their Journal.

The following papers were read:—

Note "On the Supply of Iodine from the Kelp of Guernsey," by the President.

The sea-weed from the rocky shores is largely collected by the inhabitants of the island, as is well known, laid out to dry in the fields, and afterwards burned as fuel in their houses, the ashes being kept and used as manure. These ashes are likely to contain more iodine than ordinary kelp, from being the product chiefly of the deep-sea fuci, and from the low temperature employed in the combustion of the dried plants. This was found to be the case on testing the Guernsey kelp for iodine; and the attention of manufacturers was accordingly called to it, as a source of that article which might probably be had recourse to with profit, with the present high price of that drug.

"Analysis of an ancient Peruvian Alloy," by Mr. Henry How.

The yellow metallic plate which forms the subject of the following note was obtained for analysis from Sir James Clark by Dr. Hofmann. It had been taken from a band of similar plates found surrounding the skull of a skeleton (supposed to be that of an ancient Peruvian chief or Inca) in the neighbourhood of Truxillo, in Peru.

A qualitative examination proved it to consist of gold, silver and copper.

The alloy was treated with nitric acid, and in this manner all the copper, and the greater part of the silver, were dissolved from the gold; the silver was thrown down by hydrochloric acid, and the copper precipitated from the filtrate by potassa, and weighed as black oxide. The residue left by nitric acid was treated by nitro-hydrochloric acid, the solution filtered from a little chloride of silver, and evaporated to dryness; the residue was ignited and weighed as gold, while the small portion of chloride of silver was added to the larger quantity obtained from the nitric solution.

I. 0·8722 grm. gave 0·3395 grm. of gold, 0·6340 grm. of chloride of silver, and 0·068 grm. of oxide of copper.

II. 0·94 grm. gave 0·366 grm. of gold and 0·685 grm. of chloride of silver.

Numbers which lead to the following per-centages:—

| | I. | II. |
|---|---|---|
| Gold . . . | 38·92 | 38·93 |
| Silver . . . | 54·72 | 54·82 |
| Copper . . . | 6·22 | |
| | 99·86 | |

It cannot be ascertained with certainty whether this plate consists of an artificial alloy, or is the crude product of a rough metallurgic working of an ore containing the three above-mentioned metals; the latter supposition is perhaps the more probable.

## CLXXVII. *On Gun-Cotton.*

*By* E. F. Teschemacher, *Esq.*

IN consequence of the discovery by Professor Schönbein of gun-cotton, and of the possibility of its substitution in many cases for gunpowder, I have been induced to enter into an examination of the mode of its formation and of its synthetical composition, principally with a view of ascertaining how far it would be likely to affect an important branch of trade—the production and value of saltpetre and nitrate of soda. The examination was not commenced with the view of publishing it, but some of the facts brought to light appeared to possess sufficient interest to lay before the Society. I must premise that the experiments relate only to the gun-cotton prepared by the process recommended by Mr. T. Taylor. Equal measures of nitric acid of sp. gr. 1·509, and of sulphuric acid sp. gr. 1·840, were mixed together, and constituted (No. 1) the acids used in these experiments. I dried 50 grs. of South American cotton (from La Guayra) over a water-bath, and found the cotton gave off 3·40 grs. of hygrometric water. The 46·60 grs. of cotton which remained after drying, I steeped in 487½ grs. of the mixed acids No. 1; the

strong acids were in contact with the cotton about two minutes, and after squeezing well, the cotton was washed in water to free it from the acid: the quantity of water used was 5000 grs.

The strong acid squeezed out of the cotton weighed 113½ grs. (No. 2), leaving 374 grs. of acid (No. 3) to be accounted for, to make up the original quantity used. The cotton thus prepared was perfectly dried in the air over a water-bath, and was found to weigh 79 grs., being an increase of 32·40 grs. on the cotton used, equal to an increase of 69½ grs. upon every 100 grs. of cotton in its original state.

To ascertain whether the cotton would absorb anything more, I steeped 25 grs. of the above cotton, after it had been washed and dried, in fresh acid (No. 1), but no increase of weight took place. I also steeped a fresh portion of cotton for three minutes in the same quantity of fresh acid (No. 1); it weighed after washing and drying 78 grs.; a third portion was steeped for four minutes in one-third more acid than in the previous experiments, it weighed after washing 79 grs.; so that it appeared that the cotton had taken up its maximum from the acid by the first immersion.

As these 32·40 grs. increase of weight were clearly derived from the 487½ grs. of the mixed acids, I made the following experiments to ascertain what alteration the acids had undergone.

I neutralized 100 grs. by weight of the original acid (No. 1) by carbonate of soda, and found that it required 52·80 grs. of soda for that purpose. I found likewise that to neutralize the 113½ grs. of strong acid (No. 2) separated from the cotton, required 58·52 grs. of soda, and that the remaining 374 grs. of acid to be accounted for, contained in the washings, required 170·30 grs. of soda for neutralization, making together 228·82 grs. of soda required to neutralize the 487½ grs. of acids No. 2 and 3, used for acting upon the cotton; therefore, if 100 grs. of the original mixed acids (No. 1) required 52·80 grs. of soda as above for neutralization, 487½ grs. would require (if not acted upon by the cotton) 257·36 grs. of soda; it however only required 228·82 grs. as above. The difference, 28·54 grs. of soda, is therefore equal to the acid which disappeared, or was taken up by the immersion of 46·60 grs. of cotton in the mixed acids. To ascertain whether a portion of each of the mixed acids, or only one of them, was taken up by the cotton, I added to the solution of the 100 grs. of mixed acids (No. 1) (neutralized by the soda) chloride of barium, and obtained a precipitate weighing 126 grs. of sulphate of barytes.

I also, in the same manner, precipitated from the solution

No. 2, 165·40 grs. of sulphate of barytes, and from No. 3, of 374 grs., 449·30 grs. of sulphate of barytes, making together 614·70 grs.; therefore, if 100 grs. of the original acids (No. 1) give 126 grs. of sulphate of barytes, 487½ grs. would give 614·25 grs.; they gave, as above, 614·70 grs., showing that no portion of the sulphuric acid was withdrawn, but that it was a portion of the ingredients of the nitric acid alone that combined with the cotton.

The quantity of soda neutralized by the acids (Nos. 2 and 3) was, as just stated, 28·54 grs.; therefore, if 32 grs. of soda neutralize 54 grs. of nitric acid, 28·54 grs. of soda will give 48 grs. of nitric acid, the quantity of acid which disappeared, or was taken up by the cotton.

From what took place, the following may be deduced as its synthetical composition:—48 grs. of dry nitric acid, containing 35·66 grs. of oxygen, were decomposed by the 46·60 grs. of cotton, and 32·40 grs. were added to the weight of the cotton. It is probable that the mixed acids combined with a portion of the constituent water of the cotton, which was replaced by oxygen and nitrogen, in the proportions of nitric acid, as there was no appearance of the evolution of either nitrogen or oxygen in the formation of the gun-cotton.

Its synthetical composition would stand thus:—

46·60 grs. of cotton deprived of
15·60 water, give
31·00 cotton without constitutional water, combined with
48·00 oxygen and nitrogen derived from the mixed acids,
79·00 the weight of gun-cotton produced, equal to
39·25 parts cotton,
60·75 ... oxygen and nitrogen (nitric acid)
in 100·00 parts.

From these experiments we arrive at the following conclusions regarding the formation of this substance:—That as it requires 48 grs. of nitric acid, or its equivalent 90·66 grs. of saltpetre, to form 79 grs. of gun-cotton, it will require 60·75 grs. of nitric acid, or its equivalent 114·76 grs. of saltpetre, to form 100 grs. of gun-cotton; and according to the same calculation, it will require 97·76 grs. of nitrate of soda for the same purpose.

Taking into consideration the original cost of the cotton, the expensive manipulation of the conversion of the nitre into nitric acid, and the additional weight of nitre required to produce the same weight of gun-cotton, it is evident that the latter substance must be more expensive than gunpowder, taking weight for weight of each. How far, however, gun-

cotton may exceed gunpowder in its explosive force still remains to be ascertained, and this of course forms an important element in the calculation. Other processes may be already known, or may be hereafter discovered, calculated to reduce the expenses of the formation of the so-called gun-cotton, but it must be still borne in mind that an enormous quantity of oxygen, amounting to 45 parts in every 100 parts of gun-cotton produced, must be obtained from some extraneous source for combination.

Many other vegetable fibres may be substituted for cotton; but as far as a few experiments which I have made, it appears they do not possess the explosive force of cotton. In a trial upon flax, I found that 50 grs. increased in weight to 72 grs.; the explosive force was feeble; this was the case with sawdust similarly prepared; but it is possible that this latter form of impure lignin may eventually be of more importance than it appears at present.

Fifty grains of *deal* sawdust dried at 212° were first washed with dilute muriatic acid and then with dilute caustic alkali; they were found to have lost 6 grs. after washing and again drying. The 44 grs. remaining were steeped in the mixed acids for about five minutes, then washed and dried; they increased to 58·7 grs. The acids were examined by carbonate of soda in the manner before detailed, the sawdust was found to have neutralized 22·90 grs. of soda, equal to 38·65 parts of nitric acid, or 66·66 of nitric acid for every 100 parts of gun-sawdust. This gun-sawdust flashed off readily, but with less rapidity than gun-cotton, leaving a small carbonaceous residue.

The difference in quantity of nitric acid taken up by the sawdust and the cotton is no doubt owing to the former being a much more impure form of lignin than the latter.

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November 16, 1846.—The President in the Chair.

An Address to the Members of the British Association, by Sir R. I. Murchison, 1846, was presented from the author; Taylor's Calendar of Scientific Meetings for 1846–47, from the editor.

M. Soubeiran, M. Chevalier, and F. Wrightson, Esq. were elected Members of the Society.

The following papers were read:—

"Note on the presence of Phosphoric Acid in the Felspar of Jersey." By Mr. Fownes.

In a former communication addressed to the Royal Society*, I pointed out the existence of phosphoric acid in certain rocks and

* Phil. Trans. for 1844, p. 53.

minerals of volcanic origin, as disintegrated felspar or porcelain clay, various lavas, trachytes and basalts, and volcanic tufa. Some of these rocks yielded a comparatively large quantity of phosphoric acid; others only sufficient to establish clearly the fact of its presence. I drew the conclusion that the volcanic rocks should be looked upon as the original source of the element phosphorus which plays so important a part in the œconomy of living nature, and that eruptions of lava from the depths of the earth were means appointed for renewing the fertility of the surface exhausted by the removal of phosphates and alkalies by plants.

The fundamental fact, and of course the conclusions based upon it, have been since called in question *. By the kindness of Mr. Graham, I have been enabled to repeat the experiment on a specimen of the partially-decomposed felspar of Boullay Bay, Jersey, the result of which proved quite in accordance with those above-mentioned. The same plan of examination was adopted. 1000 grains of the mineral were reduced to powder in a porphyry mortar and boiled for some time with pure dilute hydrochloric acid; water was then added, and after complete subsidence the clear liquid was decanted, evaporated nearly to dryness, and mixed with dilute ammonia in excess. The bulky precipitate obtained was washed, dried, ignited and fused with its own weight of silica and six times as much pure carbonate of soda, the melted mass disintegrated by boiling water, and the soluble portion removed by filtration. The solution was then acidulated with nitric acid, evaporated to dryness, treated with dilute solution of ammonia and filtered. The liquid so obtained, mixed with sal-ammoniac and a little sulphate of magnesia, deposited after standing a few minutes a very notable quantity of the characteristic white crystalline precipitate of ammonio-phosphate of magnesia.

The solution from which the precipitate containing the phosphates had been separated by ammonia, evaporated to dryness and ignited to expel ammoniacal salts, yielded a fixed residue containing potash in considerable quantity.

According to my observation, common felspar is one of the volcanic products poorest in phosphoric acid, and it was only in the disintegrated mineral that I succeeded in finding it at all. The unaltered felspar is too hard and compact to yield anything to hydrochloric acid, and when fused with carbonate of soda gives of necessity such an immense mass of saline matter that the trace of phosphate it probably contains is smothered and lost. Professor Kersten employed however this very mode of research by fusion with alkali, instead of simple digestion with dilute acid, which attacks with facility the lavas, trachytes, &c.

"Analysis of Sand from St. Michael's Bay, Normandy," by Mr. Gladstone.

This sand is carted away at low tide to great distances, and is employed as a manure. It consists of carbonate of lime, 44·9; salts of sea water, 0·8; organic matter, 5·2; iron, siliceous grains, and debris of granite, 49·1.

* *Pharmaceut. Central-Blatt* for 1846, p. 94.

## CLXXVIII. *On the Chemical Composition of Gun-Cotton.* *By* Messrs. Robert Porrett and E. F. Teschemacher.

IN the paper from Mr. Teschemacher read before the Society on the 2nd of November, the composition of gun-cotton, as deduced from careful synthetical experiments, was as follows:—

39·25 of cotton deprived of its constitutional water.
60·75 of dry nitric acid.
100·00

We have now to show that this composition agrees very closely with the following formula, which we have obtained from the analytical experiments that will form an important part of the present communication.

The formula in question is as follows:—$C_{12}\,H_8\,O_8 + 4NO_5$ = nitrated lignin; or in centesimal proportions,

| | | |
|---|---|---|
| Carbon | | 20·00 |
| Oxygen | 17·78 + 44·44 | 62·22 |
| Hydrogen | | 2·22 |
| Nitrogen | | 15·56 |
| | | 100·00 |

Or it may be thus described:

| | | | |
|---|---|---|---|
| Lignin dried at 350°: | Carbon | 20 | |
| | Water | 20 | = 40 |
| Nitric acid (15·56 nitrogen, 44·44 oxygen) | | | 60 |
| | | | 100 |

This, it will be seen, very nearly agrees with Mr. Teschemacher's synthetical result. We have therefore taken the composition of nitrated lignin in all our experiments as identical with that of gun-cotton.

Having by preliminary trials ascertained that with certain precautions those products might be evolved without danger and collected in close vessels, we proceed to state that our method consisted in introducing the charge of gun-cotton into a thin glass tube of about the diameter of a goose-quill, 7 inches in length, closed at one end, and bent at the other so as to be conveniently introduced under a glass receiver filled with and inverted over mercury, whilst the principal part of the tube was held in a horizontal position; the gun-cotton was exploded by heat externally applied by means of a spirit-lamp with a very small wick *to the part of the charge in the fore part of the tube*, so that its combustion proceeded backwards until the whole was consumed. The portion of the glass tube which is introduced into the mercury should

be bent at such an angle as to prevent any of the mercury entering the tube previous to combustion, and the combustion must be continuous, which is readily effected by carefully applying the heat backwards as the cotton is ignited. With these precautions, the evolution of the gas was not attended with any such violence as to interfere with its collection, nor was any portion of the charge thrown out unconsumed, which would have been the case had the heat been applied to the hinder portion first. Having collected a sufficient quantity of the gas, we passed up into it, first a little caustic potash, which absorbed the carbonic acid mixed with cyanogen gas, and then green sulphate of iron, which took up the nitric oxide; the remaining gas was mixed with half its bulk of oxygen gas, and exploded in a detonating tube, showing the quantity of carbonic oxide present; the remaining gas after the separation of the carbonic acid thus formed was considered as nitrogen.

Some of these constituents were unexpected by us, especially the cyanogen; its presence however was fully proved, as we succeeded in forming prussian blue with it. The quantity of mixed gases obtained from 52·33 grs. of gun-cotton measured 100 cubic inches; these mixed gases have the following composition:—

| | Relative volumes. | Cubic inches. | grs. | |
|---|---|---|---|---|
| Carbonic acid | 2 | 14·286 | 6·759 = | 1·815 carbon<br>4·944 oxygen |
| Cyanogen . . | 1 | 7·143 | 3·965 = | 1·815 carbon<br>2·150 nitrogen |
| Nitric oxide . | 5 | 35·715 | 11·478 = | 6·091 oxygen<br>5·387 nitrogen |
| Carbonic oxide | 5 | 35·715 | 10·714 = | 4·536 carbon<br>6·178 oxygen |
| Nitrogen . . | 1 | 7·143 | 2·154 = | 2·154 nitrogen |
| | | 100·000 | 35·070 | |

100 grs. of the same would therefore give 64·550 grs. of the mixed gases, and as the ultimate elements, 15·030 grs. of carbon, 31·680 grs. of oxygen, and 17·840 grs. of nitrogen.

By passing the gases from the combustion-tube through a tube containing fused chloride of calcium, we have separated 20 grs. of water, to be added to the gaseous products; and we observed a crystalline deposit, both in the combustion-tube and in the one leading from it, together with 5 grs. of carbon lining the combustion-tube, and resulting from the decomposition of a part of the crystalline deposits after heat-

ing the tube to redness. The weight of these together were 13·125 grs., of which 5 were carbon and 8·125 we ascertained to be anhydrous oxalic acid.

If we now collect these products, we find—

| | | | |
|---|---|---|---|
| Carbon | in the gases | 15·030 | 22·738 |
| | in the anhydrous oxalic acid | 2·708 | |
| | in the residue | 5·000 | |
| Oxygen | in the gases | 31·680 | 54·876 |
| | in the water | 17·780 | |
| | in the anhydrous oxalic acid | 5·416 | |
| Hydrogen in the water | | | 2·220 |
| Nitrogen in the gases | | | 17·840 |
| | | | 97·674 |
| Leaving a deficiency, from unavoidable errors in the experiment, of | | | 2·326 |
| | | | 100·000 |

If these ultimate elements be compared with the composition we have assigned to nitrated lignin or gun-cotton, we shall observe the following near approximation :—

| | From the analysis. | From the composition of nitrated lignin. |
|---|---|---|
| Carbon | 22·738 | 20·000 |
| Oxygen | 54·876 | 62·220 |
| Hydrogen | 2·220 | 2·220 |
| Nitrogen | 17·840 | 15·560 |
| | 97·674 | 100·000 |

Showing in the analytical result a loss of about 7 per cent. of oxygen and a gain of about 5 per cent. upon the carbon and nitrogen taken together. We have not been able to make these discrepancies disappear, but have no doubt that they result from the difficulties of the experiments, necessarily performed on very small quantities, and multiplied when brought out by calculation as 100 grains.

It occurred to us as being very desirable to add to the gun-cotton some oxidizing agent in sufficient quantity to furnish the necessary oxygen for the complete combustion of all the elements of the gun-cotton; we tried chlorate of potash with this view; we could not however get the cotton to combine with as much as we desired from an aqueous solution of the chlorate, so as to adhere to the gun-cotton uniformly; but a combustion effected with 1 gr. of the cotton with 0·4 gr. of chlorate, and by treating the residue in the tube with a further portion of chlorate, gave us the following result:—

| | | |
|---|---|---|
| Carbonic acid | 0·420 grs. | containing 0·200 carbon. |
| Carbonic oxide | 0·198 ... | |
| Nitrogen . . | 0·178 ... | |
| Water . . . | 0·200 ... | |
| | 0·996 ... | |

which differs but little from the result obtained by the imperfect combustion, and agrees completely as far as the nitrogen is concerned.

Since reading this paper an article has appeared in the *Comptes Rendus* of the Academy of Sciences at Paris, dated 23rd November 1846, that Messrs. Fordos and Gelis had obtained from gun-cotton a *cyanic compound*; this tends to confirm our discovery of the presence of cyanogen among the gaseous products.

A view may be taken of the composition of gun-cotton agreeing with the ultimate results, but arranging the elements differently, by subtracting 1 atom of oxygen from the nitric acid and adding it to the lignin; gun-cotton would then be formed of nitrous acid + oxide of lignin; this new oxide may possess alkaline properties, and thus account for the singular fact of the non-acidity of gun-cotton: we intend to try if we can establish this composition by experiment.

We have tried the action of a small galvanic battery in decomposing the gun-cotton, but without any decided results; on the first vigorous action of the battery, reddened litmus paper was made blue in the negative cell, but as the power of the battery subsided this effect disappeared. As the result of several trials, it does not appear that gun-cotton is susceptible of explosion by the discharge from a Leyden phial.

In conclusion, we think proper to express our dissent from the mechanical view taken by Mr. Crum of the nature of gun-cotton. He considers that the tubular structure which the microscope developes in cotton accounts for the admission of nitric acid into its vessels, but does not explain why it should not get out again on washing; and he thinks that the preservation of its fibrous organization is inconsistent with its chemical combination with nitric acid. Now the fact is, that when cotton is immersed in a mixture of equal measures of sulphuric and nitric acids it combines with the latter only, to the exclusion of the former, which shows a peculiar affinity inconsistent with any mechanical view of the action.

## CLXXIX. *Analysis of the Water of the Thermal Spring of Bath (King's Bath).* By Messrs. George Merck *and* Robert Galloway.

THE water of this celebrated spring, the efficacy of which was known in the time of the Romans, has been analysed repeatedly by various chemists at different periods. Richard Phillips*, Scudamore†, Walker‡, and more recently Noad§, have occupied themselves in the investigation of this water. In their several analyses, the whole amount of the fixed ingredients of the water agrees very closely; but in regard to the composition of these substances there are considerable discrepancies, as may be seen in a table which we have annexed at the end of this paper.

Besides great differences in the quantitative analysis, we find discrepancies even in regard to the presence and absence of certain constituents. Among the chemists that have been mentioned, Walker is the only one who has recognised the presence of potash. The same chemist corroborated Scudamore's statement as to the presence of magnesia, overlooked by their predecessors; but he states also that he detected alumina, which none of the others found. In all these analyses iodine has been omitted. Mr. Cuff‖ however has indicated the presence of this element in the spring.

These discrepancies made another investigation of the mineral water of Bath very desirable; the following analysis was performed at the suggestion of Dr. A. W. Hofmann.

To obtain the water genuine, and especially for the purpose of ascertaining the amount of free carbonic acid it contained, we collected the water ourselves, an operation in which we were kindly assisted by Messrs. Green and Simms, lessees of the establishment.

The water was taken from the principal well, which supplies the King's and Queen's baths, which are the most esteemed and valued in the city. Of the two other wells, one supplies the Hot Bath and the other the Cross Bath, which are in the neighbourhood of those first mentioned.

The King's Bath is an oblong cistern, 65 feet long and 40 feet broad, in which the water stands at the height of 46

* An Analysis of the Bath Water, by Richard Phillips. London, 1806.

† A Chemical and Medical Report of the properties of the Mineral Waters of Buxton, Matlock, &c., by Ch. Scudamore, M.D. 1820.

‡ Quarterly Journal of Science, Literature and Arts, vol. xxvii. 78. 1829.

§ Pharmaceutical Journal, vol. iii. 526.

‖ Memoir on the occurrence of Iodine and Bromine in certain Mineral Waters of South Britain, by Charles Daubeny; Transactions of the Royal Society of London, 1830, ii. p. 223.

inches. It is supplied from the bottom by means of twelve large and about twenty smaller apertures. By far the largest amount of water rises however from an opening made in the centre of the bath, 18 inches in diameter. Although the water flows under the influence of a very small pressure, the quantity is such, that the two reservoirs, the King's and the Queen's bath, are entirely filled in about nine hours. The quantity of water entering each minute is 126 gallons, upon the authority of Dr. Daubeny*.

## I. *Qualitative Analysis.*

The water as it issues from the well has a temperature of 46° C. (115° Fahr.), the temperature of the air being 20° C. (68° Fahr.); it is clear and without odour, and has no effect upon vegetable colours; it has a saline and slight iron taste; the iron is deposited as sesquioxide in rather large quantities in the pipes leading from the well.

The following experiments gave the qualitative composition of the mineral water; on boiling for some time a white crystalline precipitate formed. The qualitative analysis was therefore divided into two parts.

*a.* The analysis of the precipitate formed on boiling.

*b.* The analysis of the substances remaining dissolved.

### *a. Analysis of the Precipitate formed on boiling.*

1. The precipitate was treated with hydrochloric acid; a small portion of it dissolved with effervescence, indicating the presence of carbonic acid. The portion insoluble in hydrochloric acid dissolved on the addition of a large quantity of water:—*Indicating sulphate of lime.*

Another portion of the water was boiled some time, with the precaution of replacing the evaporated water, in order that all the sulphate of lime should remain in solution; in this case only a very small precipitate was formed, which was entirely soluble in hydrochloric acid.

2. On heating this solution and adding ammonia, a very slight flocculent precipitate of a yellowish-white colour was produced after some time:—*Indicating oxide of iron.*

3. In the filtrate from the sesquioxide of iron (2.), on the addition of oxalate of ammonia, a white precipitate was formed:—*Indicating salts of lime.*

4. In the liquid filtered off from the oxalate of lime (3.),

* On the Quantity and Quality of the Gases disengaged from the Thermal Spring which supplies the King's Bath in the City of Bath, by Charles Daubeny; Transactions of the Royal Society of London, 1834, I. i.

phosphate of soda produced an exceedingly slight crystalline precipitate:—*Showing the presence of magnesia.*

*Note.*—This precipitate could only be distinctly seen in testing a large quantity of the water.

*b. Analysis of the substances remaining dissolved.*

The liquid which was filtered from the precipitate (*a.*) formed on boiling had no alkaline reaction; a portion of it was evaporated nearly to dryness and treated with hydrochloric acid; no carbonic acid was evolved, from which comportment the absence of alkaline carbonates could with safety be concluded.

1. A portion of the liquid gave on addition of chloride of barium a copious white precipitate, insoluble in hydrochloric acid:—*Indicating sulphuric acid.*

2. In another portion of the liquid nitrate of silver produced a copious white precipitate, easily soluble in ammonia:—*Evidencing the presence of chlorine.*

3. The entire solubility of the silver precipitate seemed to indicate the absence of iodides. To make ourselves perfectly certain of the absence of these salts, 30 or 40 pounds of the water were evaporated to 2 or 3 pounds, and the liquid filtered off from the precipitate which had been formed; a part of this fluid was evaporated with precaution to dryness, the residue was mixed with some starch paste, and a few drops of nitric acid being added, feeble but distinct violet spots were observed: this experiment was repeated several times with the same success:—*Indicating the presence of iodine.*

4. Another portion of the liquid (*b.*) was treated with hydrochloric acid, evaporated to dryness, and gently ignited: on treating the residue with a large quantity of water an insoluble portion remained:—*Showing the presence of silicic acid.*

5. Another portion of the liquid (*b.*) gave, on addition of chloride of ammonium and oxalate of ammonia, a white precipitate:—*Indicating lime.*

6. On adding, to a portion of the filtrate, ammonia and phosphate of soda, a slight crystalline precipitate was formed:—*Indicating magnesia.*

7. For the discovery of the alkalies, the remaining portion of the filtrate from the lime precipitate was evaporated to dryness, and the residue ignited until the ammoniacal salts had been expelled. The ignited residue was then dissolved in water, the sulphuric acid and magnesia precipitated by baryta water, and after separation of the excess of baryta by means of carbonate of ammonia, the filtrate evaporated to dryness

and ignited. The residue imparted a yellow colour to the blowpipe flame:—*Evidencing the presence of soda.*

An alcoholic solution of the residue gave with a concentrated solution of bichloride of platinum a yellow crystalline precipitate:—*Indicating potassa.*

The precipitate which had formed on evaporating for the iodine determination, was treated with hydrochloric acid, the filtrate saturated with ammonia and precipitated by sulphide of ammonium; this precipitate was re-dissolved in nitro-hydrochloric acid mixed with chloride of ammonium, and the sesquioxide of iron separated by ammonia. The filtrate, evaporated and fused with nitrate of potash and carbonate of soda, gave a green mass:—*Showing traces of manganese.*

Lithia, alumina, bromine and phosphoric acid were found to be absent.

In regard to the presence of gases in the water, it was scarcely necessary to test for the presence of free carbonic acid. On mixing a solution of lime with the mineral water a precipitate was formed, which dissolved in an excess of the mineral water. The quantity of free carbonic acid however is not very large; the water has no reaction on blue vegetable colours; hydrosulphuric acid is not contained in the water. Acetate of lead gave only a white precipitate of sulphate of lead free from all trace of brown colour, which might indicate the presence of sulphur.

A large quantity of gas is continually disengaged from the chief spring as well as from the secondary ones. Dr. Daubeny* paid particular attention to the composition of this gas. He found that it consists principally of nitrogen, together with small quantities of carbonic acid and oxygen.

He employed a peculiar apparatus, constructed on purpose for these experiments, by which he was enabled to collect the whole of the gases from the principal well, as well as from those adjoining it. The experiments of Daubeny are so numerous and accurate as to preclude any other researches on the subject.

## II. *Quantitative Analysis.*

### *Determination of the Specific Gravity.*

A small bottle, which contained at the temperature of 16°·5 C. (60° Fahr.) 10 grms. of distilled water, contained at the same temperature 10·025 grms. of the mineral water; from this the specific gravity of the water is calculated as 1·0025.

* Vide Memoir mentioned.

1. *Estimation of Sulphuric Acid.*

The mineral water was heated with a little hydrochloric acid and chloride of barium added.

I. 534·199 grms. of water gave 1·340 grm. of sulphate of baryta = 0·4605 grm., or 0·08620 per cent. of sulphuric acid.

II. 475·003 grms. of water gave 1·1791 grm. of sulphate of baryta = 0·4050 grm., or 0·08526 per cent. of sulphuric acid.

Mean of the results, 0·08573 per cent.

2. *Estimation of Chlorine.*

The water was treated with nitric acid and precipitated by nitrate of silver; the precipitated chloride of silver was washed by decantation, fused and weighed.

I. 101 grms. of water gave 0·1137 grm. of chloride of silver = 0·2811 grm., or 0·02778 per cent. of chlorine.

II. 100·006 grms. of water gave 0·1093 grms. of chloride of silver = 0·02702 grms. or 0·02701 per cent. of chlorine.

Mean of the results, 0·02739 per cent.

3. *Estimation of Silicic Acid.*

To the water was added nitric acid in excess; it was then evaporated to dryness and the residue for some time heated on the sand-bath. On treating this residue with water and hydrochloric acid, the silicic acid remained behind; it was collected, washed and weighed.

I. 765·325 grms. of the water gave 0·0342 grm., or 0·00446 per cent. of silicic acid.

II. 732·015 grms. of water gave 0·0289 grm., or 0·00407 per cent. of silicic acid.

Mean of the results, 0·00426 per cent.

4. *Estimation of Iron.*

The iron was estimated,—

A. In the precipitate formed on boiling the mineral water.

B. In the water which had not been boiled.

Both estimations gave the same results.

A. Estimation of the iron in the precipitate:—

A certain quantity of the water was boiled for some time; the precipitate which had formed was washed, dissolved in hydrochloric acid and precipitated by an excess of ammonia.

I. 777·215 grms. of water gave 0·0079 grm., or 0·00101 per cent. of sesquioxide of iron.

B. Estimation of the iron in the water which had not been boiled:—

The liquid filtered off from the silicic acid (3.) was concentrated and precipitated by an excess of ammonia.

II. 765·325 grms. of water gave 0·0078 grm., or 0·00101 per cent. of sesquioxide of iron.

III. 732·015 grms. of water gave 0·0086 grm., or 0·00116 per cent. of sesquioxide of iron.

Mean of the results, 0·00106 per cent., corresponding to 0·00153 per cent. of carbonate of oxide of iron.

### 5. *Estimation of Lime.*

The estimation of the lime was divided into—

A. Estimation of the lime contained in the water in the state of carbonate.

B. Estimation of the lime contained in the water in the state of sulphate.

C. Estimation of the total amount of lime for control.

A. Estimation of the lime combined with carbonic acid:—

The ammoniacal liquor filtered off from the precipitate of sesquioxide of iron was precipitated by oxalate of ammonia; the oxalate of lime was converted in the known way into carbonate.

I. 712·747 grms. of water gave, on boiling, a precipitate containing 0·0904 grm. of carbonate of lime = 0·05062 grm., or 0·00712 per cent. of lime.

II. 623·881 grms. of water gave, on boiling, a precipitate containing 0·0782 grm. of carbonate of lime = 0·0437 grm., or 0·00700 per cent. of lime.

Mean of the results, 0·00706 per cent.

B. Estimation of the lime combined with sulphuric acid:

The mineral water was kept boiling for one or two hours, replacing the water which evaporated; the precipitate formed was filtered off, washed, and to the filtrate was added chloride of ammonium, ammonia, and oxalate of ammonia; the oxalate of lime was converted into carbonate.

I. 710·747 grms. of water gave in this way 0·6072 grm. of carbonate of lime = 0·3400 grm., or 0·04783 per cent. of lime.

II. 623·881 grms. of water gave 0·5165 grm. of carbonate of lime = 0·2892 grm., or 0·04635 per cent. of lime.

Mean of the results, 0·04709 per cent.

C. Estimation of the total amount of lime for control:—

The ammoniacal liquid which was filtered off from the precipitate of sesquioxide of iron was precipitated after the addition of chloride of ammonium by oxalate of ammonia, and the oxalate of lime converted into carbonate.

I. 765·325 grms. of water gave 0·7211 grm. of carbonate of lime = 0·403816 grm., or 0·05276 per cent. of lime.

II. 732·015 grms. of water gave 0·6981 grm. of carbonate of lime = 0·3909 grm., or 0·05340 per cent. of lime.

Mean of the results, 0·05308 per cent.

| | |
|---|---|
| Mean of the lime combined with carbonic acid | 0·00706 |
| Mean of the lime combined with sulphuric acid | 0·04709 |
| Total amount found by addition | 0·05415 |
| Mean of the total amount found by direct estimation . . . . . | 0·05308 |

### 6. *Estimation of Magnesia.*

The estimation of the magnesia was divided in the same manner as the estimation of lime into—

A. Estimation of the magnesia combined with carbonic acid.

B. Estimation of the magnesium combined with chlorine.

C. Estimation of the total amount of magnesia for control.

A. Estimation of magnesia contained in the water as carbonate:—

To the liquid filtered off from the oxalate of lime was added phosphate of soda; on stirring, after some time a precipitate of phosphate of magnesia and ammonia was formed, which was converted by ignition into pyrophosphate of magnesia.

I. 777·215 grms. of water gave, on boiling, a precipitate which contained 0·0046 grm. of pyrophosphate of magnesia = 0·001685 grm., or 0·00021 per cent. of magnesia.

II. 623·881 grms. of water gave, on boiling, a precipitate which contained 0·0044 grm. of pyrophosphate of magnesia = 0·00016 grm., or 0·00025 per cent. of magnesia.

Mean of the results, 0·00023 per cent.

B. Estimation of the magnesia contained in the water as chloride of magnesium.

The liquid filtered off from the oxalate of lime was concentrated by evaporation, ammonia added filtered off from a small portion of silicic acid which separated, and the magnesia precipitated by phosphate of soda.

I. 414·279 grms. of water gave in this way 0·1007 grm. of pyrophosphate of magnesia = 0·03689 grm., or 0·008906 per cent. of magnesia.

II. 427·1 grms. of water gave 0·1050 grm. of pyrophosphate of magnesia = 0·03846 grm., or 0·009004 per cent. of magnesia.

Mean of the results, 0·008955 per cent.

C. Estimation of the total amount of magnesia for control:—

The liquid filtered off from the precipitate of oxalate of lime was concentrated, ammonia and phosphate of soda added.

I. 765·325 grms. of water gave 0·1936 grm. of pyrophosphate of magnesia = 0·070929 grm., or 0·00926 per cent. of magnesia.

II. 732·015 grms. of water gave 0·1837 grm. of pyrophosphate of magnesia = 0·0673 grm., or 0·00919 per cent. of magnesia.

Mean of the results, 0·00922 per cent.

| | |
|---|---|
| Mean of the magnesia combined with carbonic acid | 0·00023 |
| Mean of the magnesia contained in the water as chloride of magnesium . . . . . | 0·00895 |
| Total amount found by addition | 0·00918 |
| Mean of the total amount found by direct estimation | 0·00922 |

### 7. *Estimation of the Alkalies.*

For the estimation of the alkalies the mineral water was evaporated to one-third of its volume and baryta water added in excess, the precipitates of sulphates of baryta, lime, magnesia and sesquioxide of iron were filtered off, and the excess of baryta precipitated by means of carbonate of ammonia. To get rid of the silicic acid the filtrate was evaporated to dryness with hydrochloric acid, gently ignited, dissolved in water, again filtered and evaporated to dryness; the mixed chlorides obtained in this manner were weighed.

I. 632·481 grms. of the mineral water gave 0·2937 grm. of chloride of sodium and chloride of potassium = 0·04643 per cent. of the mixed chlorides.

II. 546·032 grms. of water gave 0·2538 grm. of chlorides of sodium and potassium = 0·04648 per cent. of the mixed chlorides.

Mean of the results, 0·04645 per cent.

### 8. *Estimation of the Potassa.*

The chlorides of potassium and sodium were dissolved in a small quantity of water and an excess of bichloride of platinum added; the liquid was then evaporated to dryness in the water-bath, the residue digested with alcohol, the insoluble chloride of platinum and potassium filtered off from the soluble sodium salt and washed with alcohol; the precipitate was dried in the water-bath and weighed.

I. 632·481 grms. of the mineral water, or 0·2987 grm. of the mixed chlorides, gave 0·124 grm. of chloride of platinum

and potassium = 0·0378 grm. of chloride of potassium = 0·00597 per cent. of chloride of potassium, which equals 0·00377 per cent. of potassa.

II. 546·032 grms. of water, or 0·2538 grm. of the mixed chlorides, gave 0·0975 grm. of chloride of platinum and potassium = 0·02977 grm. of chloride of potassium = 0·00545 per cent. of chloride of potassium, which equals 0·00342 per cent. of potassa.

Mean of the results, 0·00571 per cent. of chloride of potassium and 0·0359 per cent. of potassa.

### 9. *Estimation of the Soda.*

The quantity of soda was found simply by the difference of the mixed chlorides and the quantity of chloride of potassium found by direct estimation.

| | |
|---|---|
| Mean of the mixed chlorides . . . | 0·04645 |
| Mean of the chloride of potassium . | 0·00571 |
| Chloride of sodium . . | 0·04074 |

corresponding to 0·02168 per cent. of soda.

### 10. *Estimation of Carbonic Acid.*

To find the quantity of free carbonic acid contained in the water at the moment it was taken from the well, a syphon of exactly known capacity was immersed in the well, and the water obtained in this way put in bottles, containing a mixture of ammonia and chloride of calcium. In this way the free carbonic acid as well as the carbonic acid in combination was precipitated in the form of carbonates. Four bottles were filled with mineral water by this method. The capacity of the siphon was exactly 533 cubic centimetres, therefore $533 \times 4 \times 1{\cdot}0025 = 2137$ grms. of water were taken.

The precipitate from the water contained in these four bottles was collected, washed, dried and weighed; it yielded 1·4748 grm. of carbonate mixed with some alumina from impurity in the solution of chloride of calcium.

To estimate the quantity of carbonic acid in this precipitate, two portions of it were taken and estimated separately after the method proposed by Drs. Fresenius and Will.

I. 0·66 grm. of the carbonate, &c. gave in this way 0·22 grm. of carbonic acid, therefore 1·4748 grm. of the carbonate, or 2137·0 grms. of water, gave 0·4916 grm. of carbonic acid.

II. 0·718 grm. of the carbonate, &c. gave 0·23 grm. of carbonic acid, therefore 1·4748 grm. of the carbonate, &c., or 2137·0 grms. of water, gave 0·4718 grm. of carbonic acid.

*Mean of the results.*

0·4817 grm. of carbonic acid, which equals 0·02254 per cent.

| | | |
|---|---|---|
| Total amount of carbonic acid . . | | 0·02254 |
| Carbonic acid existing in combination— | | |
| With oxide of iron . . . | 0·00057 | |
| With lime . . . . . | 0·00554 | |
| With magnesia . . . . | 0·00024 | |
| Sum total . . . . . | | 0·00635 |
| Free carbonic acid remaining | | 0·01619 |

From the details contained in the preceding pages, it follows that the thermal spring in the King's Bath contains the following constituents in 100 parts:—

| | |
|---|---|
| Carbonate of lime . . . . | 0·01260 |
| Carbonate of magnesia . . | 0·00047 |
| Carbonate of oxide of iron . | 0·00153 |
| Sulphate of lime . . . . | 0·11436 |
| Sulphate of potassa . . . | 0·00663 |
| Sulphate of soda . . . . | 0·02747 |
| Chloride of sodium . . . | 0·01806 |
| Chloride of magnesium . . | 0·02083 |
| Silicic acid . . . . . | 0·00426 |
| | 0·20620 |

Traces of manganese and iodine.

*Estimation of the total amount of the fixed ingredients in the water for control.*

The water was concentrated in a porcelain dish, and afterwards evaporated to dryness in a platinum basin. The residue was heated in an air-bath until the weight was constant. Two estimates were made.

I. 217·058 grms. of water gave 0·4540 grm., or 0·20916 per cent. of residue.

II. 319·57 grms. of water gave 0·6726 grm., or 0·21040 per cent. of residue.

Mean of the results, 0·20978 per cent.

But in this experiment the iron was obtained in the state of sesquioxide, whilst in the preceding calculation it is taken as the carbonate of the oxide, in which form it exists in the water.

On calculating the absolute weights from the above, we obtain the following numbers:—

| | In a litre. | In an imperial gallon (70,000 grs.). |
|---|---|---|
| Carbonate of lime . . . | 0·1260 grm. | 8·82000 grs. |
| Carbonate of magnesia . . | 0·0047 ... | 0·32900 ... |
| Carbonate of oxide of iron . | 0·0153 ... | 1·07100 ... |
| Sulphate of lime . . . . | 1·1436 ... | 80·05200 ... |
| Sulphate of potassa . . . | 0·0663 ... | 4·64100 ... |
| Sulphate of soda . . . . | 0·2747 ... | 19·22900 ... |
| Chloride of sodium . . . | 0·1806 ... | 12·64200 ... |
| Chloride of magnesium . . | 0·2083 ... | 14·58100 ... |
| Silicic acid . . . . . | 0·0426 ... | 2·98200 ... |
| | 0·20621... | 144·01800 ... |

According to our experiments, 1 litre of the water contains 95·64 cubic centimetres of free carbonic acid at the temperature of 46° C. (115° F.) and normal atmospheric pressure.

One imperial gallon contains therefore 26·45 cubic inches of free carbonic acid of 46° C., being more than double the quantity which has been determined by former experiments.

This however is not surprising, as the estimations previously made had been effected by the expulsion of the carbonic acid from the water. Besides the difficulty of avoiding a loss of carbonic acid before the operation, it is scarcely possible, as Mr. Phillips justly notices in his paper, to expel all carbonic acid by simple ebullition. Besides, we see from the experiments of Daubeny, that the gas which escapes from the well contains at different periods highly varying amounts of carbonic acid. He found by several experiments that the King's Bath evolves on an average 267 cubic inches of gas per minute, or 223 cubic feet in twenty-four hours. He further ascertained that this gas consists nearly entirely of nitrogen, mixed with a small amount of oxygen and carbonic acid, and that these gases were generally in the following proportion:—

| | |
|---|---|
| Nitrogen . . | =91·9 |
| Oxygen . . . | = 3·8 |
| Carbonic acid | = 4·3 |

In many instances, however, he observed as much as 7·4 to 8·2, and even once 11·5 parts of carbonic acid.

From these observations there is no doubt that the quantity of carbonic acid dissolved in the water is very variable.

In the following Table we give the analyses of former experimenters, calculated in an imperial gallon (70,000 grs.).

| | Phillips. | Scudamore*. | Walker. | Noad. |
|---|---|---|---|---|
| Carbonate of lime ..... | 7·680 | 5·280 | 10·667 | |
| Carbonate of oxide of iron | 0·274 | 0·200 | 0·243 | 0·521 |
| Carbonate of soda ..... | ..... | ..... | ..... | 5·760 |
| Sulphate of lime ..... | 86·400 | 98·320 | 81·624 | 96·240 |
| Sulphate of potassa ..... | ..... | ..... | 2·927 | |
| Sulphate of soda ..... | 14·400 | 1·520 | 19·371 | |
| Chloride of sodium ..... | 31·680 | 12·240 | 15·122 | 27·456 |
| Chloride of magnesium ... | ..... | 15·360 | 13·339 | 7·142 |
| Alumina ..... | ..... | ..... | 0·150 | |
| Silicic acid ..... | 1·960 | 1·920 | 3·233 | 3·360 |
| | 142·394 | 134·840 | 146·676 | 140·479 |
| Quantity directly observed | 144·125 | ..... | 147·622 | 149·72 |
| Carbonic acid..... | 11·52 cub. in. | ..... | 7·60 cub. in. | |

Our analysis agrees, as may be seen, best with that of Walker. According to Professor Liebig's† arrangement of mineral waters, the thermal spring of Bath would belong to the saline waters containing carbonic acid.

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Dec. 7, 1846.—The President in the Chair.

J. W. Griffiths, M.D. was elected an Associate of the Society.

The following papers were read:—

## CLXXX. *On the Metaphosphates.*

*By* Robert Maddrell, *Esq.*

HAVING had my attention drawn to a new method for preparing pure phosphoric acid from bone-ash, proposed by Professor Gregory, and a new and apparently anomalous phosphate of magnesia, accidentally discovered by him whilst trying to obtain the above-mentioned acid pure by heating at a temperature above 600° F.‡, I was induced at the suggestion, and with the kind assistance of Professor von Liebig, to repeat the process, and also to prepare a quantity of the salt, and subject it to analysis. The general results I have found are as follows:—If phosphoric acid, freed from lime and sulphuric acid §, be heated to a temperature above 600° F., it deposits a white substance, having all the general physical characters of the new salt, but in which I found on analysis 22·47 per cent. of magnesia, corresponding to the metaphosphate of magnesia ($MgO\ PO_5$). After a considerable quantity of this substance had been deposited, I digested the mass in

* Recalculated according to a more correct principle by Walker.

† *Handwörterbuch der Chemie*, Art. 'Analyse der Mineralwasser.'

‡ See Transactions of the Royal Society of Edinburgh.

§ See Geiger's *Handbuch der Pharmacie*.

water, filtered, and evaporated the solution, and again heated the acid to upwards of 600° F., under the impression that it might still contain the new compound; by continuing this heat for half an hour, I again obtained a quantity of metaphosphate of magnesia; and it was not until after a third repetition of this process that I obtained Professor Gregory's compound, in which I found on analysis 16·276 per cent. of magnesia, corresponding to the quantity found by that chemist in his salt; but on estimating the quantity of phosphoric acid present, I only obtained 75·25 per cent. of $PO_5$, leaving a loss of upwards of 8 per cent. Being convinced that another base must be present, from the enormous loss, I proceeded further with my analysis and found the presence of soda, which gave me 8·146 per cent. of soda.

This salt therefore is not an anomalous phosphate of magnesia, but a double metaphosphate of magnesia and soda, in the proportions are 3 equivs. of metaphosphate of magnesia and 1 equiv. of metaphosphate of soda, $3(MgO, PO_5) + NaO, PO_5$. It is nearly insoluble in hydrochloric acid and aqua regia, but soluble in concentrated sulphuric acid.

The analysis of the salt was made as follows:—I dissolved the salt in pure concentrated sulphuric acid, then diluted the solution with water, and precipitated the magnesia by an excess of ammonia; from the precipitate, after being heated to redness, was estimated the quantity of magnesia. To the filtered solution was added a solution of a salt of magnesia (with proper precautions) to precipitate the remainder of the phosphoric acid, and from this precipitate, as well as the former, was estimated the quantity of the $PO_5$. A second quantity was taken for the determination of the soda, which was dissolved in concentrated sulphuric acid, diluted with water, and precipitated by an excess of ammonia. The filtered solution, containing phosphoric acid, was then precipitated by acetate of lead, the excess of lead by sulphuretted hydrogen, and the soda in the solution evaporated and estimated as a sulphate, which gave me the following results:—

*Analysis*, No. I.

| | | | | | Per cent. |
|---|---|---|---|---|---|
| ·897 grm. substance gave | ·399 | $2MgO, PO_5$ | ·146 | MgO = | 16·276 MgO |
| ·897 ... ... | 1·065 | ... | ·675 | $PO_5$ = | 75·250 $PO_5$ |
| ·712 ... ... | ·133 | NaO $SO_3$ | ·058 | NaO = | 8·146 NaO |
| | | | | | 99·672 |

No. II.

| | | | | | Per cent. |
|---|---|---|---|---|---|
| 1·16 grm. substance gave | ·511 | $2MgO, PO_5$ | = ·187 | MgO = | 16·12 MgO |
| 1·16 ... ... | 1·386 | ... | = ·878 | $PO_5$ = | 75·689 $PO_5$ |
| 1·23 ... ... | ·228 | NaO, $SO_3$ | = ·099 | NaO = | 8·048 NaO |
| | | | | | 99·857 |

| | | Found. | |
|---|---|---|---|
| Reckoned. | Atom. | I. | II. |
| 16·368 = | 3 MgO | 16·276 | 16·12 |
| 75·376 = | 4 $PO_5$ | 75·250 | 75·689 |
| 8·256 = | NaO | 8·146 | 8·048 |
| 100·000 | | 99·672 | 99·857 |

Formula, $3(MgO, PO_5) + NaO, PO_5$.

The different result obtained by Professor Gregory no doubt arose from the method upon which his examination of this salt was conducted, viz. by determining the amount of magnesia present, and considering the loss on the weight of substance used to represent phosphoric acid, and probably from not thinking at the time of the presence of a salt of soda in bones.

With regard to the phosphoric acid prepared as above, after the salt has ceased to form, I find that it is not yet quite pure, but contains traces of magnesia as well as soda, and therefore this process will always yield an acid containing more or less of these substances.

Under the impression that the phosphoric acid obtained by this process was pure, I attempted to prepare with it the metaphosphates of nickel and cobalt, by adding the sulphates of these bases to an excess of the acid, and heating as before to upwards of 600° F., with the idea that they might be deposited in a somewhat similar manner to the metaphosphate of magnesia. This I found on analysis not to be the case, as the salts which I obtained in this way were not the pure metaphosphates, but double salts in combination with soda, closely allied in their composition to Gregory's salt.

The nickel compound obtained in this way was deposited in the form of a greenish-yellow, anhydrous powder, insoluble in water and diluted acids, but soluble in concentrated sulphuric acid.

The analysis of this salt was made by fusing with carbonate of soda, and treating the fused mass with water to separate the metallic oxide from the alkaline phosphate. A second quantity was taken for the determination of soda, which I dissolved in concentrated sulphuric acid, then diluted with water, and precipitated the solution containing phosphoric acid by acetate of lead, and the excess of lead in the filtered solution by sulphuretted hydrogen. To the filtered solution was then added an excess of ammonia with sulphuret of ammonium to precipitate the nickel, and the solution containing soda was evaporated and determined as a sulphate.

| | | Found. Per cent. | Atom. | Reckoned. Per cent. |
|---|---|---|---|---|
| ·853 grm. substance gave ·254 NiO | | = 29·789 | 6NiO | = 29·805 |
| 2·24 ... ... ... ·231 $NaO, SO_3$ = ·091 | NaO = | 4·062 | NaO | = 4·134 |
| | $PO_5$ estimated as loss = | 66·149 | $7PO_5$ | = 66·061 |
| | | 100·000 | | 100·000 |

Formula, $6(NiO, PO_5) + NaO, PO_5$.

The cobalt salt is a beautiful rose-coloured, anhydrous compound, insoluble in water and dilute acids, but soluble in concentrated sulphuric acid.

The analysis was made by dissolving it in concentrated sulphuric acid, diluting with water, and precipitating by an excess of ammonia and sulphuret of ammonium. The sulphuret was then redissolved in nitric acid, and the solution diluted with water, filtered and precipitated by caustic potash. A second quantity was taken for the determination of the soda, and estimated as the preceding salt of nickel.

| | | Found. Per cent. | Atom. | Reckoned. |
|---|---|---|---|---|
| 1·24 grm. substance gave ·403 $Co_3O_4$ | = ·3755 CoO = | 30·282 | 6NiO | = 29·775 |
| 1·12 ... ... ... ·117 $NaO, SO_3$ = ·051 | NaO = | 4·358 | NaO | = 4·136 |
| | $PO_5$ estimated as loss = | 65·460 | $7PO_5$ | = 66·089 |
| | | 100·000 | | 100·000 |

Formula, $6(CoO, PO_5) + NaO, PO_5$.

Thinking I might still obtain the pure metaphosphates of nickel and cobalt in the way above mentioned, I prepared a quantity of pure phosphoric acid by the oxidation of phosphorus with nitric acid, and the process, when tried with the acid prepared in this way, perfectly succeeded.

By this method I obtained also the metaphosphates of MnO, $Al_2O_3$, $Fe_2O_3$, $Cr_2O_3$, CuO, BaO, SrO, CaO, KO, NaO, though not in every case using the sulphates of the bases, as I find that almost any other salt will do equally well.

*Metaphosphate of Oxide of Nickel.*—This salt I obtained on adding a solution of sulphate of nickel to an excess of pure phosphoric acid, and by evaporating the mixture in a platinum vessel until the sulphuric acid had been expelled, then by heating it to upwards of 600° F., when it deposited as a greenish-yellow, anhydrous compound. It is insoluble in water, hydrochloric acid and aqua regia, but soluble in concentrated sulphuric acid.

The determination of the nickel was made as the preceding salt of nickel, and the phosphoric acid estimated from the loss.

| | Found. Per cent. | Atom. | Reckoned. Per cent. |
|---|---|---|---|
| 1·565 grm. substance gave ·537 NiO = | 34·401 | NiO = | 34·485 |
| $PO_5$ as loss = | 65·599 | $PO_5$ = | 65·515 |
| | 100·000 | | 100·000 |

Formula, $NiO, PO_5$.

*Metaphosphate of Oxide of Cobalt* was obtained by the same process as the preceding salt of nickel. It is a beautiful rose-coloured, anhydrous compound, insoluble in water and diluted acids, but soluble in concentrated sulphuric acid.

The analysis was made by dissolving in concentrated sulphuric acid, diluting with water, and precipitating by an excess of ammonia and sulphuret of ammonium. The sulphuret was redissolved in nitric acid, the solution diluted with water, filtered, and precipitated by caustic potash. The $PO_5$ was estimated from the loss.

| | Found. Per cent. | Atom. Reckoned. |
|---|---|---|
| ·983 grm. substance gave ·367 $Co_3 O_4$ = ·342 CoO = | 34·791 | CoO = 34·452 |
| $PO_5$ as loss = | 65·209 | $PO_5$ = 65·548 |
| | 100·000 | 100·000 |

Formula, $CoO, PO_5$.

*Metaphosphate of Protoxide of Manganese.*—This salt was obtained in a similar manner to the preceding salts of nickel and cobalt. It is a white, anhydrous compound, insoluble in water and dilute acids, but soluble in concentrated sulphuric acid.

The determination of the manganese was made as in the preceding salt of cobalt, and the $PO_5$ estimated from the loss.

| | Found. Per cent. | At. Reckoned. Per cent. |
|---|---|---|
| ·857 grm. substance gave ·306 $MnO, Mn_2O_3$ = ·2847 MnO = | 33·22 | MnO = 33·321 |
| $PO_5$ as loss = | 66·78 | $PO_5$ = 66·679 |
| | 100·00 | 100·000 |

Formula, $MnO, PO_5$.

*Metaphosphate of Alumina* was obtained by dissolving alumina in an excess of phosphoric acid, evaporating, and heating up to the same temperature as with the preceding salts. It is a white, anhydrous compound, insoluble in water and concentrated acids.

The analysis for the determination of alumina was made, according to Berzelius's method, by fusing the salt with $1\frac{1}{2}$ part of silicic acid and 6 parts of carbonate of soda; and the $PO_5$ estimated from the loss.

| | Found. Per cent. | Atom. | Reckoned. |
|---|---|---|---|
| 1·253 grm. substance gave ·243 $Al_2 O_3$ = | 19·392 | $Al_2 O_3$ = | 19·352 |
| $PO_5$ as loss = | 80·607 | $3PO_5$ = | 80·648 |
| | 100·000 | | 100·000 |

Formula, $Al_2 O_3, 3PO_5$.

*Metaphosphate of Peroxide of Iron.*—This salt was obtained on the addition of perchloride of iron to an excess of diluted phosphoric acid, and by evaporating and heating up to the same temperature as before; it is insoluble in water and diluted acid, but soluble in concentrated sulphuric acid.

The analysis was made by fusing the salt with carbonate of soda, then by treating the fused mass with water, to separate the peroxide of iron from the alkaline phosphate, and the phosphoric acid estimated from the loss.

| | Found. Per cent. | Atom. | Reckoned. |
|---|---|---|---|
| ·850 grm. substance gave ·224 $Fe_2O_3$ = | 26·353 | $Fe_2O_3$ = | 26·767 |
| $PO_5$ as loss = | 73·647 | $3PO_5$ = | 73·233 |
| | 100·000 | | 100·000 |

Formula, $Fe_2O_3$, $3PO_5$.

*Metaphosphate of Oxide of Chromium* was obtained by dissolving oxide of chromium in an excess of diluted phosphoric acid, evaporating, and heating up to the same temperature as before. It is a beautiful green, anhydrous compound, insoluble in water and concentrated acids.

The analysis was made by fusing the salt with caustic potash; the fused mass was then digested in water (to separate the oxide of chromium from the alkaline phosphate), filtered, and the filtered solution neutralized with hydrochloric acid. To the solution was added ammonia, chloride of ammonium, and a salt of magnesia, to precipitate the phosphoric acid, and from the precipitate, after being heated to redness, the quantity of the latter was estimated. The $Cr_2O_3$ I was obliged to estimate as loss, as I found it exceedingly difficult to obtain a correct result, it being more or less oxidized by the action of the caustic potash.

| | Found. Per cent. | Atom. | Reckoned. |
|---|---|---|---|
| ·67 grm. substance gave ·772 MgO, $PO_5$ = ·488 $PO_5$ = | 72·836 | $3PO_5$ = | 72·731 |
| $Cr_2O_3$ as loss = | 27·164 | $Cr_2O_3$ = | 27·269 |
| | 100·000 | | 100·000 |

Formula, $Cr_2O_3$, $3PO_5$.

*Metaphosphate of Oxide of Copper* was obtained on adding a solution of nitrate of copper to an excess of diluted phosphoric acid, and evaporating and heating up to the same temperature as before. It is a bluish-white, anhydrous compound, insoluble in water and diluted acids, but soluble in concentrated sulphuric acid. This salt I dissolved in concentrated sulphuric acid, diluted the solution with water, and precipitated by sulphuretted hydrogen; the sulphuret was then redissolved in hydrochloric acid, diluted with water, filtered, and precipitated by caustic potash, and the $PO_5$ estimated from the loss.

| | Found. | Atom. | Reckoned. |
|---|---|---|---|
| 1·518 grm. substance gave ·542 CuO = | 35·704 | CuO = | 35·713 |
| $PO_5$ as loss = | 64·296 | $PO_5$ = | 64·287 |
| | 100·000 | | 100·000 |

Formula, CuO, $PO_5$.

*Metaphosphate of Barytes* was obtained by decomposing

carbonate of barytes in diluted phosphoric acid, then evaporating and heating it up to 600° F.; it is insoluble in water, hydrochloric acid and aqua regia, but decomposed by concentrated sulphuric acid. This salt was heated with concentrated sulphuric acid, digested in water, and filtered, and the $PO_5$ estimated from the loss.

| | Found. Per cent. | Atom. Reckoned. |
|---|---|---|
| 1·236 grm. substance gave ·974 BaO, $SO_3$ = ·639 BaO = | 51·70 | BaO = 51·746 |
| $PO_5$ as loss = | 48·30 | $PO_5$ = 48·254 |
| | 100·00 | 100·000 |

Formula, BaO, $PO_5$.

*Metaphosphate of Strontian.*—This compound was obtained by decomposing carbonate of strontian in diluted phosphoric acid, evaporating and heating as before; it is insoluble in water, hydrochloric acid and aqua regia, but decomposed by concentrated sulphuric acid.

This salt was heated with concentrated sulphuric acid, and then the mass digested in water, mixed with alcohol, and filtered. The $PO_5$ was estimated from the loss.

| | Found. Per cent. | Atom. Reckoned. |
|---|---|---|
| 1·014 grm. substance gave ·755 SrO, $SO_3$ = ·425 SrO = | 41·913 | SrO = 42·043 |
| $PO_5$ as loss = | 58·087 | $PO_5$ = 57·957 |
| | 100·000 | 100·000 |

Formula, SrO, $PO_5$.

*Metaphosphate of Lime.*—This compound was obtained in a similar manner to the salts of barytes and strontian. It is a white, anhydrous powder, insoluble in water and diluted acids, but decomposed by concentrated sulphuric acid. The analysis of this salt was made the same as the salt of strontian.

| | Found. | Atom. Reckoned. |
|---|---|---|
| ·806 grm. substance gave ·550 CaO, $SO_3$ = ·2284 CaO = | 28·337 | CaO = 28·52 |
| $PO_5$ as loss = | 71·663 | $PO_5$ = 71·48 |
| | 100·000 | 100·00 |

Formula, CaO, $PO_5$.

*Metaphosphate of Magnesia* was obtained by dissolving carbonate of magnesia in an excess of diluted phosphoric acid, evaporating, and heating as before; it may also be obtained by preparing phosphoric acid from bone-ash, according to the above-mentioned process. It is a white, anhydrous compound, insoluble in water and diluted acids, but soluble in concentrated sulphuric acid. This compound was dissolved in pure concentrated sulphuric acid, diluted with water, and precipitated by an excess of ammonia. The filtered solution containing the remainder of the phosphoric acid was preci-

pitated (with the proper precautions) by a salt of magnesia and estimated accordingly.

| grm. | | Found. Per cent. | Atom. Reckoned. |
|---|---|---|---|
| 1·887 substance gave 1·157 | 2MgO, $PO_5$ = ·424 | MgO = 22·47 | MgO = 22·453 |
| ... ... ... 2·307 | ... = 1·46 | $PO_5$ = 77·424 | $PO_5$ = 77·547 |
| | | 99·894 | 100·000 |

Formula, MgO, $PO_5$.

*Metaphosphate of Potash.*—This salt was obtained by igniting strongly together equal parts of chlorate of potash and phosphoric acid (of a syrupy consistence), and by digesting the mass in water to separate the soluble part from the insoluble. It is an anhydrous compound, nearly insoluble in water, but soluble in diluted as well as concentrated acids. The acetic solution gives a white precipitate with nitrate of silver. This insoluble compound is decomposed on being treated with solutions of nitrate of silver, acetate of lead, and chloride of barium, into the metaphosphates of these metallic oxides.

This compound was dissolved in acetic acid, diluted with water, and the $PO_5$ in the solution precipitated by acetate of lead, and the excess of lead in the filtered solution by sulphuretted hydrogen. The solution containing potash was then evaporated, and the potash determined as nitrate.

| | Found. | Atom. Reckoned. |
|---|---|---|
| 1·468 grm. substance gave 1·25 KO, $NO_5$ = ·582 KO = | 39·645 | KO = 39·8 |
| $PO_5$ estimated as loss = | 60·355 | $PO_5$ = 60·2 |
| | 100·000 | 100·0 |

Formula, KO, $PO_5$.

*Metaphosphate of Soda* was obtained by igniting strongly together equal parts of nitrate of potash and phosphoric acid (of a syrupy consistence), and by digesting in water to separate the soluble from the insoluble part. It is an anhydrous compound, nearly insoluble in water, but soluble in diluted and concentrated acids. The solution in acetic acid gives a white precipitate with nitrate of silver; it is also decomposed on being treated with the same salts as the salt of potash. This salt was dissolved in acetic acid, diluted with water, and the $PO_5$ precipitated in the solution (with proper precautions) by a salt of magnesia.

| | Found. | Atom. Reckoned. |
|---|---|---|
| ·943 grm. substance gave 1·042 MgO, $PO_5$ = ·659 $PO_5$ = | 69·883 | $PO_5$ = 69·537 |
| NaO estimated as loss = | 30·117 | NaO = 30·463 |
| | 100·000 | 100·000 |

Formula, NaO, $PO_5$.

## CLXXXI. *On the Amount of Sulphur and Phosphorus in various Agricultural Crops. By* Henry Clifton Sorby, *Esq.*

HAVING thought it highly probable that in the ordinary method of estimating the amount of sulphur and phosphorus in plants, viz. by burning them and analysing their ashes, there might be in many cases a loss from portions being rendered volatile by contact with combustible matter at a high temperature, I was induced to commence a series of analyses, employing a method against which there was no such objection, and, as will be seen, the quantities really present in various plants are much greater than has been hitherto anticipated. Having obtained a proper specimen, one portion of known weight was dried at 212° F. and weighed, and another in precisely the same condition was employed for the analysis, the amount which I generally used varying with the dryness of the substance from 200 grs. to 500 grs., which was cut into pieces if necessary, and introduced into a flask, and carefully heated with pure nitric acid, a little water being added if the substance was a dry one. No large quantity of the acid is required, and a gentle heat is kept up until the whole is digested down into a yellowish pulpy mass; water is then added, the whole boiled, and when cold filtered and washed, there being invariably a quantity of white fibrous substance left undissolved. To the yellowish solution thus obtained nitrate of baryta was next added, and though at first perhaps no precipitate was formed, sulphate of baryta was gradually deposited, and after standing for a day or so, the precipitate was collected on a filter, washed, dried, ignited and weighed, from which the amount of sulphur was calculated. It is well to ascertain whether it is pure sulphate of baryta, by adding to it after weighing a little hydrochloric acid, since sometimes there was present a little carbonate, which of course produces effervescence, and when that is the case, which seldom occurred to any but the most trifling extent, the amount is easily ascertained and a proper deduction made, to obtain the true weight of the sulphate alone.

To the solution filtered as above, I next added acetate of lead in moderate quantity, and then caustic ammonia in slight excess, filtered and washed the precipitate. When dry this precipitate was carefully calcined in a porcelain crucible over a lamp, at as low a temperature as convenient, stirring with a glass rod until the whole was converted into a mixture of metallic lead, oxide and phosphate of lead. These were then dissolved in nitric acid, and ammonia added until a consider-

able precipitate of subnitrate was formed, when on adding acetic acid the whole of the phosphate alone was left insoluble, which, after standing awhile, was collected on a filter, washed, dried, ignited and weighed, and the amount of phosphorus obtained by calculation. That this method is correct, and that the phosphate which is thus obtained is $Pb_3 P O_8$, I have proved by experiment.

It must be borne in mind that the amounts given below are those of sulphur and phosphorus, I having thought it right to give them as such, and not as sulphuric and phosphoric acids, since most certainly they do not exist invariably as such or as their salts in plants, and I therefore see no reason why they should not be given as elements, like the amounts of carbon, nitrogen, oxygen and hydrogen as usually given in such analyses.

The plants analysed, with only three exceptions, viz. the rye, mangel-wurzel, and hops, were obtained from the fields in which they were growing by myself, and hence I can vouch for their freedom from impurities, and have no doubt the others were as much so as possible.

Table of the Amounts of Sulphur and Phosphorus in various Agricultural Crops, calculated in 100 parts, dried at 212° F. until the weight remained constant.

| Name of Plant, &c. | Sulphur. | Phosphorus. |
|---|---|---|
| Four species of grass (*Poa palustris* and *trivialis*, *Festuca pratensis*, *Cynosurus cristatus*) | ·165 | ·164 |
| Rye grass (*Lolium perenne*) | ·310 | ·183 |
| Italian rye grass | ·329 | ·145 |
| Red clover (*Trifolium pratense*) | ·107 | ·149 |
| Ditto | ·087 | ·131 |
| Very fine white clover (*T. repens*) | ·099 | ·183 |
| Ordinary ditto | ·151 | ·139 |
| Very fine trefoil (*Medicago lupulina*) | ·136 | ·052 |
| Lucern (*M. sativa*) | ·274 | ·046 |
| Ditto | ·452 | ·215 |
| Ditto | ·293 | ·353 |
| Lints (*Vicia sativa*) | ·178 | ·183 |
| Kidney potatoes (*Solanum tuberosum*) | ·094 | ·213 |
| Ditto, tops | ·389 | ·357 |
| Ditto, fruit | ·071 | ·597 |
| American native potatoes | ·082 | ·212 |
| Ditto, tops | ·206 | ·483 |
| Carrot (*Daucus carota*) | ·092 | ·255 |
| Ditto, tops | ·745 | ·382 |
| Mangel-wurzel (*Beta altissima*) | ·058 | ·190 |
| Ditto, tops | ·502 | ·293 |
| Early yellow-top turnip (*Brassica rapa*) | ·351 | ·352 |
| Ditto | ·421 | ·346 |
| Ditto, tops | ·758 | ·360 |
| Ditto | ·615 | ·380 |

| Name of Plant, &c. | Sulphur. | Phosphorus. |
|---|---|---|
| Swede turnip (*Brassica oleracea*) | ·435 | ·172 |
| Ditto, tops | ·458 | ·250 |
| Rape (*B. oleifera*) | ·448 | ·233 |
| Drum-head cabbage (*B. campestris*) | ·431 | ·267 |
| Wheat plant entire (*Triticum vulgare*) when just gone out of flower | ·151 | ·248 |
| Ditto | ·170 | ·140 |
| Ear of wheat when the grain was formed, but milky | ·075 | ·271 |
| Straw from the above | ·240 | ·132 |
| Ear of wheat when ripe | ·090 | ·336 |
| Straw from the above | ·213 | ·043 |
| Red wheat | ·070 | ·363 |
| Ditto, straw | ·293 | ·079 |
| White wheat from the same field as the above red | ·054 | ·366 |
| Ditto, straw | ·207 | ·112 |
| Wheat (another sample) | ·051 | ·410 |
| Ditto, chaff | ·091 | ·252 |
| Very fine barley (*Hordeum distichum*) | ·066 | ·498 |
| Ditto, straw | ·390 | ·087 |
| Rather poor barley | ·040 | ·367 |
| Ditto, straw | ·191 | ·065 |
| Barley plant when in flower | ·313 | ·236 |
| Oat plant (*Avena sativa*) when just coming into flower | ·226 | ·194 |
| Ditto in flower | ·189 | ·189 |
| Green oats | ·125 | ·317 |
| Straw of ditto | ·329 | ·128 |
| Black tartarian oats | ·080 | ·381 |
| Straw of ditto | ·271 | ·110 |
| White oats | ·090 | ·334 |
| Straw of ditto | ·401 | ·153 |
| White oats (another sample) | ·074 | ·382 |
| Straw of ditto | ·195 | ·057 |
| Rye ears (*Secale cereale*) when young | ·073 | ·076 |
| Straw of ditto | ·099 | ·153 |
| Rye | ·051 | ·160 |
| Bean plant (*Vicia faba*) in flower | ·045 | ·258 |
| Beans | ·071 | ·600 |
| Ditto, straw | ·148 | ·233 |
| Peas (*Pisum sativum*) | ·158 | ·206 |
| Ditto, straw | ·214 | ·076 |
| Fine hops (*Humulus lupulus*) | ·127 | ·574 |
| Bind of ditto | ·091 | ·138 |

From the above analyses it will be seen how very much the amounts vary in some cases, whereas in others they are pretty constant. This variation may probably be occasioned by that of the amount of phosphates and sulphates in the soils. I have observed as a general rule, that the finer the quality of the specimen the larger the proportions of sulphur and phosphorus present; though in the case of lucern, in which the phosphorus varies as much as in any crop of which I have analysed a sufficient number of specimens to be able to give an opinion, all the samples were growing luxuriantly. It may be presumed that when the amounts vary so much,

without apparently affecting the growth of the plant, the particular constituent so varying is not of such importance for the plant as when more constant.

It will be observed that in many plants different parts require different constituents, which indeed is well known; as for instance in the case of wheat it is probable that an abundance of sulphates in the soil would produce fine straw, and of phosphates, fine grain, and the converse, other necessary constituents being present.

It may also, perhaps, be inferred from these analyses that when grain is growing and ripening the amount of phosphorus increases in greater proportion than the total weight, and diminishes in the straw, the grain abstracting that constituent from it. Similar inferences may perhaps be derived from the above, many of which are given for such purposes.

The table given below is a practical application of these analyses, being intended to show the quantities of gypsum and bone-phosphate of lime represented by the sulphur and phosphorus which are removed annually from an acre of land by the respective crops; being also that which should be added to already fertile land to maintain it in that condition. No allowance for what would be removed by drainage is made, as that is too uncertain in its quantity, and cannot in many cases be at all material, or else uncultivated natural lands would long ago have become sterile. The quantities so removed are no doubt compensated for by the disintegration of the substrata, and the superficial removal of exhausted soil by washing.

In such a calculation as this, however, it is affectation to pretend to great exactness, the elements which unavoidably enter into it being so variable. The quantities on which I have calculated are the greatest which are shown in the analyses, unless where the variations are given, when I have taken the extremes, and the weight of crop per acre is what I learn to be a medium between the very best and average crops; but I am most willing to confess that I am not myself practically acquainted with this part of my subject, and hence cannot answer for their absolute correctness, but have obtained them from the best authorities accessible to me. The necessary alterations, however, are easily made by any one for himself, from the data I have given, but I think they cannot be far wrong. The quantities are pounds of gypsum and bone-phosphate of lime removed from one acre.

| Name of Crop, &c. | Weight per acre of crop in tons. | Gypsum. | Bone-phosphate. |
|---|---|---|---|
| Hay | 2 | 34 to 67 | 26 to 32 |
| Clover hay (one crop) | 2½ | 29 | 35 |
| Clover, green (whole crop) | 15 | 45 | 53 |
| Lucern | 12 | 93 to 152 | 14 to 103 |
| Lints | 8 | 34 | 31 |
| Wheat | 210 st. | 7 to 10 } 45 to 65 | 44 to 50 } 51 to 68 |
| Ditto, straw | 1¾ | 38 to 55 } | 7 to 18 } |
| Barley | 190 st. | 8 } 70 | 55 } 67 |
| Ditto, straw | 1½ | 62 } | 12 } |
| Oats | 220 st. | 13 } 49 to 88 | 48 } 56 to 73 |
| Ditto, straw | 1¾ | 36 to 75 } | 8 to 25 } |
| Beans | 200 st. | 10 } 30 | 69 } 96 |
| Ditto, straw | 1¼ | 20 } | 27 } |
| Peas | 200 st. | 21 } 54 | 24 } 36 |
| Ditto, straw | 1½ | 33 } | 12 } |
| Rye | 180 st. | 6 } 27 | 17 } 45 |
| Ditto, straw | 2 | 21 } | 28 } |
| Potatoes | 10 | 23 } 97 | 46 } 126 |
| Ditto, tops | 10 | 74 } | 80 } |
| Carrots | 20 | 26 } 72 | 64 } 85 |
| Ditto, tops | 3 | 46 } | 21 } |
| Mangel-wurzel | 30 | 27 } 51 | 76 } 88 |
| Ditto, tops | 4 | 24 } | 12 } |
| Swede turnips | 20 | 104 } 132 | 36 } 49 |
| Ditto, tops | 4 | 28 } | 13 } |
| Early yellow-top ditto | 18 | 81 } 129 | 59 } 80 |
| Ditto, tops | 5 | 48 } | 21 } |
| Rape | 20 | 140 | 64 |
| Cabbage | 20 | 88 | 47 |

## CLXXXII. *Observations on the oxidizing power of Oxygen when disengaged by means of Voltaic Electricity.* By H. Kolbe, *Esq., Ph.D.*

IN describing in a former paper * the properties of sesquichloro-carbohyposulphuric acid, I stated that this body resists the action of the most powerful oxidizing agents, such as chromic acid, nitric acid, and even nitro-hydrochloric acid. I likewise stated the change it undergoes by the action of a voltaic current, when an easily oxidizable metal is used for the positive pole. By this means another copulated acid is produced, in which one or more equivalents of chlorine are replaced by corresponding proportions of hydrogen.

I have since observed that this acid is completely decomposed on employing two platina plates as electrodes; by which arrangement oxygen is disengaged at the positive pole. The following details, which contain a more perfect account of this observation, I hope will be acceptable to the Society.

* Liebig's *Annalen der Chemie*, liv. pp. 156, 160.

On decomposing a concentrated solution of sesquichloro-carbohyposulphate of potash by a strong voltaic current (obtained by four elements of Bunsen's battery), at the commencement no hydrogen can be observed at the negative pole in consequence of the formation of the above-mentioned copulated acids, whilst chlorine, carbonic acid, and afterwards oxygen, are evolved at the positive pole. At the moment decomposition commences a distinct acid reaction of the solution is perceptible, owing to the formation of free hydrochloric and sulphuric acids; in a later stage of the process, these acids increasing in quantity, hydrogen appears at the negative pole, until finally, after all the hydrochloric acid has been decomposed, and the disengagement of chlorine has ceased, small octahedral crystals of perchlorate of potash are deposited from the solution, which now contains a large amount of free sulphuric acid and bisulphate of potash. The formation however of perchloric acid in this process is always preceded by that of chloric acid; for on evaporating the solution in an earlier stage of the decomposition, beside the before-mentioned octahedral crystals, the well-known rhombic plates of chlorate of potash are obtained.

The following formula represents the most probable decomposition sesquichloro-carbohyposulphuric acid undergoes by the action of a voltaic current:—

$$KO + C_2 Cl_3 S_2 O_5 \left\{ \begin{array}{l} KO + Cl\,O_7 \\ 2SO_3 \\ 2CO_2 \\ 2Cl. \end{array} \right. \Big\} 12O$$

The production of perchloric acid in an acid solution is certainly a fact worthy of attention, for according to all the observations hitherto made, combination between chlorine and oxygen could only be effected in presence of a free alkaline basis ready to unite with the newly-formed acid; but ascertained as it is by a great number of careful experiments, it is another proof of the unparalleled negative power of oxygen when evolved by means of voltaic action.

These observations induced me to make the following experiments.

A neutral solution of chloride of potassium was decomposed in the same manner by a strong voltaic current; it immediately became alkaline, whilst hydrogen and chlorine were disengaged. The formation of chlorate of potash, which took place under these circumstances, can evidently be considered only as the result of the ordinary chemical action of chlorine upon caustic potash. On mixing however a solution of chloride of potassium with sufficient sulphuric acid to set free all the

muriatic acid, and passing the voltaic current through it as before, chlorate of potash was nevertheless formed, which was subsequently converted into perchlorate of potash.

The transformation of oxy-acids of chlorine, such as liquid hypochloric acid ($ClO_4$), or of a solution of chlorate of potash, into perchloric acid by means of voltaic action, has been mentioned by Berzelius. I have ascertained, moreover, that when a voltaic current is passed through hypochloric acid, especially when previously mixed with some sulphuric acid, free chloric and perchloric acids are formed, after the disengagement of a considerable quantity of chlorine.

A concentrated solution of chloride of ammonium evolves hydrogen at the negative pole but neither oxygen nor chlorine at the positive pole. But the surface of the platina plate representing the latter pole is covered with small yellowish oily drops of chloride of nitrogen, which as soon as the two poles are brought into contact decomposes with a more or less violent explosion, chlorine and nitrogen being evolved. This experiment illustrates at once the formation of this compound and its highly explosive character.

Cyanide of potassium if dissolved in water is easily oxidized by a voltaic current, and converted into cyanate of potash, but I did not succeed in obtaining a percyanate of potash. I was not more successful in endeavouring to form a fluorate of potash from the fluoride of potassium by the same means.

I have not prosecuted my experiments further upon inorganic substances, having from some observations on the behaviour of organic compounds under the action of the voltaic current obtained results of so much greater interest, as to induce me to give them my exclusive attention; and at a future time, when I have completed the investigation, I shall beg leave to communicate it to the Chemical Society.

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December 21, 1846.—The President in the Chair.

Mr. Button presented Specimens of Bromide of Potassium and Chloride of Copper to the Museum.

Messrs. F. Field and J. Wonfor were elected Members.

The following papers were read:—

## CLXXXIII. *On the existence of a New Vegeto-Alkali in Gun-Cotton.* *By* Robert Porrett, *Esq.*

At the last meeting of this Society on the 7th instant, a joint communication from Mr. Teschemacher and myself "On the Chemical Composition of Gun-Cotton" was read, and in the last paragraph but one thereof I suggested that a view

might be taken of the arrangement of its elementary particles which would account for the singular fact of its non-acidity, by supposing it a compound of nitrous acid and oxide of lignin, the said new oxide being also supposed to possess alkaline properties.

It was before mentioned that the action of a small voltaic battery on gun-cotton gave but very slight indications of its decomposition, but that slight as they were they were rather favourable to the suggestion; the indifference of this compound to the electrical action of the battery I found was owing to its highly non-conducting nature, but I succeeded rather better by moistening the gun-cotton with acetic acid, and placing it in a thin layer between a plate of silver and one of zinc, completing the circuit with a copper wire and leaving them for forty-eight hours so arranged; at the end of that time, on dismounting this little voltaic arrangement, the inner surface of the silver plate was found to be encrusted with a small quantity of matter, which when dry looked white like starch, which powerfully restored the blue colour of reddened litmus paper, and which when heated to redness left a black carbonaceous residue; the minute quantity obtained made further experiments with it impossible, but it increased my desire to be able to procure the same substance by chemical means in any quantity that might be wanted.

After several trials I succeeded by the following process.

I took 2 ounces by measure of nitric acid of the specific gravity 1·45, to which I added 50 grains of gun-cotton; the mixture being gradually heated to 100° of Fahrenheit's scale and kept below 180°, became quite transparent and fluid, and all the cotton disappeared, being quietly dissolved without any evolution of gas; when a portion of the solution in this state was dropped into water a white precipitate was formed, having all the properties, structure excepted, of the original gun-cotton, the liquid was therefore a simple solution in acid, without decomposition; but on heating the liquid further up to 240°, deep red acid vapours were given off abundantly for a long time, and these collected in a receiver surrounded with ice proved to be hyponitrous acid. The same effect exactly took place when sulphuric acid was used instead of nitric at the same temperature, so that the hyponitrous acid was merely eliminated in both cases, and not formed from the excess of nitric acid used in the former instance; the cold and very concentrated nitric solution containing a great excess of acid was now brought nearly, but not quite, towards a neutral state by pouring into it a strong solution of subcarbonate of potash, after which a solution of bicarbonate of potash was used

until perfect neutrality was obtained: the liquid in this state became thickened, not only by the quantity of minute crystals of nitrate of potash formed in it beyond what it could hold in solution, but also by an abundant precipitate of a whitish-gray colour, consisting of the new alkali probably in a state of carbonate. The liquid was heated nearly to ebullition, during which its colour became darker, and it was set aside in order that the crystals of nitrate of potash formed on cooling might be separated and the liquid disembarrassed of them as much as possible; after this it was evaporated to dryness by the heat of a water-bath, and the brownish residue was acted upon first by sulphuric æther, which however would not dissolve any portion of it; next by alcohol, specific gravity 0·813, which took up a very small quantity of the new alkali; then spirit of wine was tried; the solvent power was greater than that of the alcohol, but it had the disadvantage of taking up with the alkaline matter a very minute quantity of the nitrate of potash which accompanied it, so that I could not get an exclusive solvent for the former; the principal quantity by far of the carbonated alkaline oxide of lignin still remained, and I was obliged to use a small quantity of cold, distilled water for its solution, notwithstanding that the water took up at the same time some of the nitrate of potash and bicarbonate of potash remaining in the mass. This aqueous solution contains the new alkali in abundance, but mixed as stated with the other two salts, it acts very powerfully upon reddened litmus paper.

When a portion of the hyponitrous acid is neutralized by an aqueous solution of the new alkali, hyponitrite of oxide of lignin, probably identical with gun-cotton or with xyloidine, is reproduced and precipitated as an insoluble compound.

Thus I have verified the accuracy of my suggestion, excepting that instead of nitrous acid neutralized by a new alkali existing in gun-cotton, it is the hyponitrous acid so neutralized that constitutes that substance. For this new alkali I have proposed the name *Lignia*, and believe that it opens a wide field for scientific research.

I suspect that in the natural decay of woody fibre from leaves and rotting plants this alkali is produced in combination with acetic acid, and that the acetate of lignia so formed exists in the sap of all vegetables; further, that it is decomposed and deoxidated by light acting on the leaves and bark of trees, reproducing lignin for the assimilation and growth of the plant: its action also on the animal system deserves inquiry. I lay no stress however on these speculations, excepting so far as they may stimulate others to enter into in-

vestigations which it is impossible for me, consistently with my other duties, to find time for carrying on, and I leave the subject without reserve to those who have more leisure.

I would remark, that the composition of lignia must be that of lignin plus 2 atoms of oxygen given up by the nitric acid in becoming hyponitrous acid; and I would further observe, that the latter acid and lignia forming an insoluble compound, may probably be employed as mutual tests of each other's presence in combinations.

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## CLXXXIV. *On some new Researches in Animal Chemistry. Extracted from a Letter from* Professor Liebig *to* Dr. A. W. Hofmann.

I AM at present occupied with the investigation of the constituents of the animal fluids which are found without the blood and lymphatic vessels. The fluid from flesh, for example, reacts strongly acid, and the question was, whence arose this acidity? After overcoming more difficulties than I have ever experienced in any investigation, I have for the first time indisputably proved that free lactic and phosphoric acid exist in the whole organism wherever muscle is found. How curious, that in the absence of all proofs on the part of the opponents of lactic acid, I should now demonstrate to them its existence in the flesh of oxen, fowls, calves, and sheep, by preparing and analysing the most beautifully crystallized zinc and lime salts! How wonderful, that in the animal organism acids and alkalies are found separated by a membrane, constituting myriads of little galvanic circles, which, as such, must produce chemical and electrical effects! To the latter class I refer all the observations of Matteucci, which can now be easily explained.

I have further found that the flesh of the muscles of oxen, fowls, sheep, calves, and the carnivorous pike contain creatin, prepared by Chevreul eleven years ago, and which, from Berzelius's not being able to reproduce it, has since then, in a measure, disappeared from the field of science. Creatin is a beautiful substance, having the formula $C_8 N_3 H_{11} O_6$. At the temperature of 100° C. it loses 2 equivs. of water, and becomes $C_8 N_3 H_9 O_4$ = glycocoll + ammonia or caffein + amidogen and water. Heated in a stream of hydrochloric acid, creatin loses 4 equivs. of water and takes up 1 of hydrochloric acid. By this treatment, however, its nature is entirely altered, being now converted into a beautiful organic base, the properties of which are totally different from those

of creatin. It becomes now soluble in water, and forms with bichloride of platinum a fine crystallized double salt.

I have, finally, discovered two other new bodies in the same fluids, of which the one crystallizes in needles, the other in plates of the lustre of mother-of-pearl. Unfortunately I have obtained scarcely sufficient for two analyses from 40 lbs. of the flesh of oxen and 20 of that of fowls.

I see a boundless field before me, and doubt not that for every *quality* of the animal body, something which can be estimated *quantitatively*, will also be discovered to which it is indebted for its properties.

I have also satisfied myself as to the part which common salt plays in the bodies of animals. I have found that the fluids without the blood and lymphatic vessels contain only potash-salts, viz. chloride of potassium and phosphate of potash, with phosphate of magnesia, whilst the blood and lymph contain merely those of soda (phosphate of soda). If, therefore, the latter are indispensable to the formation of blood and the processes of life, it is evident that an animal on the continent, which finds in plants only potash-salts, should have chloride of sodium given to it, by means of which the phosphate of potash of the seeds and of the rest of the plant is transformed into chloride of potassium and phosphate of soda. I found further that the salt brine which flows from salted meat contained certainly alkaline phosphates, and that scurvy is hence easily explained by the deficiency in the salted meat of the alkaline phosphates necessary to the formation of blood. The soup from boiled meat contains the soluble phosphates of the flesh, and the meat itself the insoluble. Neither the soup nor the flesh alone can maintain the processes of life, but both must be taken together. The English have in this respect hit upon the proper practice. In a theoretical point of view their food is more correctly combined than that of the Germans.

Still more wonderful results have been obtained by the oxidation of casein by means of peroxide of manganese and sulphuric acid, by M. Gugelberger. Three products are obtained: the first of which is aldehyde, the second oil of bitter almonds, and the third a fluid æthereal body with a composition similar to metacetone. The aldehyde was analysed as aldehydite of ammonia, of which a considerable quantity was obtained. From oil of bitter almonds the most beautiful benzoic acid was produced by the action of chlorine.

From these results a sort of conception may be obtained how and wherefore many medicines have a certain deleterious or useful action.

Urea, creatin, glycocoll, leucin, cystin, &c. are organic bases, and only products of the animal body or its elements, and organic bases are partly poisonous, partly beneficial in their action. I have caused the new experiments of Mulder on his protein to be repeated. The substance prepared by Fleitmann in this laboratory, according to his new method, and supposed to be free from sulphur, still contains 1·5 per cent., as does likewise a similar preparation by Laskowski.

I beg of you to communicate this short notice to the Chemical Society, of which I have the honour to be a member.

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## CLXXXV. *On the Salts of Sulphurous Acid.*

*By* J. Sheridan Muspratt, *Esq., Ph.D.*

I HAVE been induced to return to this subject by a paper lately published by Dr. Rammelsberg in Poggendorff's *Annalen* *. In his treatise he differs slightly from me in the quantities of water contained in some of the sulphites, but as he invariably took his water as loss and as mine was generally determined by combustion with chromate of lead, I did not think it worth while going over all the analyses that I had performed in Giessen, being so thoroughly convinced of the accuracy of those results. The only point where we materially disagree is regarding the constitution of the red sulphite of copper, and which will be subsequently discussed under that head. When I first undertook, in Baron Liebig's laboratory, the investigation of the salts of sulphurous acid, very little was known of their constitution; but since that time they have occupied the attention of numerous chemists, and are now invested with as much interest as the compounds of any other acid. They are very readily decomposed either by moisture or heat, and on this account may have led different chemists to the assumption of various formulæ for the same salt. For example, there is scarcely any salt of this acid which does not contain traces of sulphate, which are always overlooked in the analysis; and moreover, unless great care is exercised in oxidizing the sulphurous acid when its quantity is to be determined, serious errors may arise. I shall now proceed to the description of the sulphites under their respective heads.

*Sulphite of Soda.*—This salt is obtained by transmitting sulphurous acid through a solution of carbonate of soda until the liquid becomes acid, and then allowing the solution to

* lxvii. pp. 245, 391; or No. 89 of the Chemical Gazette, July 1, 1846, p. 254.

repose for some days under a bell-jar over sulphuric acid. The crystals possess a cooling and sulphurous taste, and are slightly alkaline to test-paper.

*Analysis*:—7·10 grs. burned with chromate of lead gave 4·19 grs. of water = 59·01 per cent.

Formula, $NaO, SO_2 + 10$ aq.

Vauquelin has described a sulphite of soda of the following constitution:—$NaO, SO_2 + 8$aq; and Rammelsberg analysed one which agreed with the annexed formula: $NaO, SO_2 + 7$aq. The varying proportions of water can only be accounted for by the different temperatures at which the salts have been formed.

*Bisulphite of Soda.*—Dr. Rammelsberg obtained an acid salt agreeing with the formula $2(NaO, 2SO_2)$ + aq. I find however on referring to his results that the formula $Na\,SO_2 + HO\,SO_2$, which I gave in my former paper, corresponds quite as well with his numbers as the one given by him.

*Sulphite of Ammonia.*—I have not yet succeeded in procuring from an aqueous solution an ammoniacal sulphite of sufficient stability for analysis. The salts formed in alcohol and æther, and heretofore described*, possessed the subjoined formulæ:—

$$NH_4O, SO_2 + \text{aq.}$$
$$NH_4O, SO_2 + SO_2.$$

I have produced another ammonia sulphite by passing sulphurous acid into a very strong solution of caustic ammonia until there was no smell either of the acid or alkali, and then adding cautiously absolute alcohol. After a short time a brilliant white saline mass of crystals subsided, which were allowed to remain undisturbed for twenty-four hours. I threw the whole on to a filter and dried the crystals over sulphuric acid. This salt is alkaline, and evolves traces of ammonia.

*Analysis*:—23·09 grs. of the salt gave 33·88 grs. sulphite of barytes = 9·32 sulphurous acid or 40·36 per cent.

The formula $2(NH_4O, SO_2) + NH_3 + 3$aq. requires 40·09 per cent. sulphurous acid.

*Sulphites of the Protoxide of Iron.*—Finely divided metallic iron dissolves pretty readily in sulphurous acid, imparting to the liquid a slight green tinge. When this liquid is evaporated *in vacuo*, very small and almost colourless crystals are obtained, which are but slightly soluble in water. Exposed to the air in a dry state they are not readily altered, but if moist are rapidly converted into sulphate. I found my sulphurous acid, on analysing this compound, to agree so closely

* *Ann. Chem. und Pharm.*, Bd. l. p. 285.

with what Fordos and Gelis had previously given, that I neglected determining the iron and water. 5·65 grs. gave 7·00 grs. sulphate of barytes = 1·92 grs. sulphurous acid or 33·98 per cent. Centesimally represented,—

| | | Theory. | F. & G. | Mean. |
|---|---|---|---|---|
| 1 eq. protoxide of iron | 439·21 | 37·28 | 37·23 | |
| 1 ... sulphurous acid . | 401·17 | 34·06 | 34·04 | 33·98 |
| 3 ... water . . . . | 337·44 | 28·76 | 28·73 | |
| | 1177·82 | 100·00 | 100·00 | |

Formula, $FeO, SO_2 + 3$ aq.

*Sulphites of the Peroxide of Iron.*—When sulphurous acid is passed through water holding in suspension freshly-precipitated peroxide of iron, the whole readily dissolves, and the liquid acquires a blood-red colour, which disappears on exposure to the air. If this solution be boiled so as to expel the uncombined acid, and then left to the atmospheric action for some days, it acquires a light brownish colour, and deposits a reddish brown compound containing sulphurous acid and peroxide of iron. Dr. Kœne of Brussels expresses the constitution of this salt by the formula

$$Fe_2O_3, SO_2 + 7aq.$$

I found that when caustic potash was added very gradually to the blood-red solution above-mentioned, a yellowish crystalline precipitate formed, the liquid remaining still acid. This compound, after filtration, edulcoration and desiccation, gave the following results :—

9·01 grs. gave 2·18 grs. peroxide of iron.

6·21 grs. gave 6·80 grs. sulphate of barytes = 1·87 grs. sulphuric acid.

10·11 grs. gave 1·50 gr. water.

Composition per cent. :—

| | | Theory. | Found. |
|---|---|---|---|
| 3 eqs. Sulphurous acid. | 1203·51 | 30·66 | 30·11 |
| 2 ... Potash . . . . | 1179·84 | 30·06 | |
| 1 ... Peroxide of iron. | 978·42 | 24·93 | 24·19 |
| 5 ... Water . . . . | 562·50 | 14·35 | 14·83 |
| | 3924·27 | 100·00 | |

These numbers agree with the formula

$$Fe_2O_3SO_2 + 2(KO, SO_2) + 5aq.$$

This double sulphite of iron and potash appears to be Kœne's salt, in which 2 equivalents of water are replaced by 2 equivalents of sulphite of potash.

The sulphite of the peroxide of iron forms a salt with sulphite of ammonia, but it is very difficult to get a sufficient

quantity of it for analyses. It contains 33·68 per cent. of peroxide of iron.

*Sulphites of Nickel.*—The two salts which I described in my first paper on the sulphites possessed the subjoined formulæ :—

$$NiO, SO_2 + 4aq.$$
$$NiO, SO_2 + 6aq.$$

The latter agrees with the results of Fordos, Gélis and Rammelsberg. I have again prepared the former by transmitting a stream of sulphurous acid gas into water holding in suspension carbonate of nickel. When the whole had dissolved, the solution was filtered and boiled, which liberated a mass of small greenish crystals, almost insoluble in water.

6·02 grs. salt burned with chromate of lead gave 2·08 grs. water = 34·55 per cent.

The formula $NiO, SO_2 + 4$ aq. affords 34·06 per cent. of water.

Dr. Böttinger has described a double sulphite of nickel of the following constitution :—

$$NiO, SO_2 + NH^4O, SO_2 + 4 aq.$$

*Sulphites of Cadmium.*—Carbonate of cadmium in water is readily dissolved by sulphurous acid, and when the resulting solution is treated with absolute alcohol an aluminous-looking precipitate appears, which when dried and heated in a test-tube affords no water—it must be the anhydrous sulphite of cadmium. If however the gelatinous precipitate is allowed to remain in the alcoholic menstruum for some days it disappears, and there deposit in its stead beautiful silvery-looking crystals, which turn out to be the same salt as that obtained by Fordos and Gélis when dissolving the metal in the acid.

*Analysis* :—6·79 grs. of salt gave 6·94 grs. sulphate of barytes = 1·90 sulphurous acid.

8·11 grs. salt gave 1·29 grs. water.

Centesimally represented,—

| | Theory. | Found. | |
|---|---|---|---|
| 1 eq. Sulphurous acid . . | 401·17 | 28·19 | 27·98 |
| 1 ... Oxide of cadmium . | 796·77 | 55·99 | |
| 2 ... Water . . . . . | 224·96 | 15·82 | 15·90 |
| | 1422·90 | 100·00 | |

Formula, $CdO, SO_2 + 2aq.$

It is oxidized very slowly when exposed to the air in a dry state; is sparingly soluble in water, and readily dissolved by dilute acids. I have not formed any double salts with the sul-

phite of cadmium. Dr. Rammelsberg analysed a salt which gave him the annexed formula,—

$$2(CdO, SO_2) + NH^3.$$

*Sulphites of Copper.*—The brilliant red salt which is formed either by boiling together solutions of sulphate of copper and sulphite of ammonia, or passing sulphurous acid into water, holding in suspension oxide of copper, was first analysed by Chevreul, whose numbers agree with the formula—

$$3Cu_2O, 4SO_2 + 5aq.$$

I gave the annexed formula for this salt,*—

$$Cu_2O, SO_2 + aq.$$

Böttinger† analysed the compound after me, and his results favour the formula—

$$3Cu_2O, 4SO_2 + 4aq.$$

Rammelsberg however has stated that the salt is a double one, and constituted as follows:—

$$CuO, SO_2 + Cu_2O, SO_2 + 2aq.$$

I have reprepared the red salt by passing a stream of sulphurous acid into water containing pure oxide of copper. When the whole had dissolved, the liquid was boiled. The red compound deposited in pretty large crystals, which were thrown upon a filter and effused with cold water *until the filtrate did not afford the slightest milkiness with a solution of chloride of barium.* They were then dried *in vacuo.* I tested the salt for *sulphuric acid* before submitting it to analysis, and found traces present, even after taking every precaution.

*Analyses.*

| | | | Per cent. |
|---|---|---|---|
| I. | 8·84 grs. gave | 9·30 BaO, $SO_3$ = 2·55 | $SO_2$ = 28·84 |
| II. | 7·41 ... | 8·32 BaO, $SO_3$ = 2·28 | $SO_2$ = 30·76 |
| III. | 6·52 ... | 7·11 BaO, $SO_3$ = 1·95 | $SO_2$ = 29·90 |
| IV. | 9·62 ... | 10·03 BaO, $SO_3$ = 2·759 | $SO_2$ = 28·68 |
| V. | 18·47 ... | 20·71 BaO, $SO_3$ = 5·69 | $SO_2$ = 30·80 |
| I. | 13·41 grs. salt with | PbO, $CrO_3$ gave 1·38 | HO = 10·29 |
| II. | 11·13 ... ... | PbO, $CrO_3$ ... 0·97 | HO = 8·71 |
| III. | 10·74 ... ... | PbO, $CrO_3$ ... 1·02 | HO = 9·49 |

Mean of the above per cent.

| | |
|---|---|
| Sulphurous acid . . . | 29·796 |
| Water . . . . . | 9·496 |
| Base or loss . . . . . | 60·708 |
| | 100·000 |

* *Ann. Chem. und Pharm.*, bd. l. p. 285.
† Ibid. bd. li. p. 412.

The copper has also been determined in the salt by my brother Frederick and myself.

| | | Per cent. |
|---|---|---|
| F. M. | 6·94 grs. salt gave 4·70 CuO | $=4·22$ $Cu_2O=60·80$ |
| Dr. M. | 11·41 ... ... 7·48 CuO | $=6·72$ $Cu_2O=58·88$ |

It is evident from the preceding results, *that if the base of this salt be only suboxide of copper*, its constitution may be assumed as the following,—

$$Cu_2O, SO_2 + aq.$$

Dr. Rammelsberg found the annexed quantities of sulphurous acid,—

35·12 35·06 34·47,

which I can only account for by his salt not being so well washed as mine. My salt dissolves in hydrochloric acid, affording a colourless liquid, and when a weak solution of potash is added to this, a white precipitate subsides. Yellow prussiate of potash gives a whitish precipitate in the acid solution, soluble in an excess of muriatic acid. When the red salt is placed on a filter and affused with boiling water until the filtrate affords no milkiness with barytes, half of its sulphurous acid is removed.

7·37 grs. gave 4·41 grs. $BaO, SO_3 = 1·21$ $SO_2 = 16·41$ per cent.

This quantity favours the formula—

$$2(Cu_2O, HO)\ SO_2.$$

Böttinger states in his paper, "That by long boiling with the liquid this salt loses sulphurous acid and becomes lighter in colour, which confirms my own observation. The analysis of such a precipitate gave me 66·60 per cent. of $Cu_2O$, which will account for the varying results obtained by different chemists when analysing this red salt."

*Sulphite of Copper and Soda.*—When rather strong solutions of sulphate of copper and sulphite of soda are mixed together and treated with absolute alcohol, a dark reddish-looking liquid, which greatly resembles nitrobenzide, subsides, and if this be collected and left *in vacuo* for some time, fine yellow crystals appear, which after washing and desiccation afforded the subjoined results:—

| | | | Per cent. |
|---|---|---|---|
| 16·40 grs. salt gave | 7·27 grs. HO | | $=44·32$ |
| 15·17 ... ... | 1·81 ... CuO | $=1·62$ | $Cu_2O=10·67$ |
| 6·13 ... ... | 5·44 ... $BaO, SO_3$ | $=1·49$ | $SO_2 = 24·30$ |

These numbers agree very closely with the formula—

$$Cu_2O, SO_2 + 5(NaO, SO_2) + 38aq,$$

if there was no uncombined sulphite of soda present.

Represented per cent.—

| | | Theory. | Found. |
|---|---|---|---|
| 1 eq. | Suboxide of copper | 891·39 | 9·36 | 10·67 |
| 6 ... | Sulphurous acid . | 2407·02 | 25·62 | 24·44 |
| 5 ... | Soda . . . . . | 1954·50 | 20·52 | |
| 38 ... | Water. . . . . | 4274·24 | 44·50 | 44·32 |
| | | 9527·15 | 100·00 | |

This salt, when heated in a test-tube, first gives off large quantities of water, then sulphurous acid, and the residue consists principally of sulphates of copper and soda, with traces of sulphur, &c.

*Sulphite of Copper and Ammonia.*—I mixed a solution of sulphate of copper with a large excess of sulphite of ammonia, then put the mixture into a long wide tube containing a thermometer, and applied heat. I removed the solution from the sand-bath at 136° F., because at this temperature silvery-looking flakes began to deposit, which powerfully refracted the light. In a short time a large quantity of a shining compound had separated, which when dried over sulphuric acid and submitted to analysis gave the annexed results:—

8·690 grs. salt gave 10·73 sulphate of barytes = 2·952 grs. sulphurous acid = 33·97 per cent.

As these numbers agreed so closely with Böttinger's formula*,—

$$2(Cu_2O, SO_2) + NH^4O, SO_2 + 3aq,$$

I thought further determinations unnecessary. When this compound is heated with water, it is decomposed and the red gritty salt separates. Great care is required in the preparation of this sulphite, for it is difficult to prevent some of the red salt depositing with it. The best way to obtain it in large quantities, is to heat slightly a strong solution of sulphate of copper with an excess of bisulphite of ammonia, then cork the vessel and allow the mixture to remain undisturbed for some days.

All the sulphurous acid for my experiments was obtained by the deoxidation of sulphuric acid by means of metallic copper,—

$$2SO_3 + Cu = CuO, SO^3 + SO^2.$$

* Liebig's *Annalen*, bd. li. p. 411.

## CLXXXVI. *Analysis of the Bohemian Glass as found in the Combustion Tubes employed in Organic Analysis.* By Mr. Thomas Rowney.

THE difficultly fusible variety of Bohemian glass has been repeatedly the subject of chemical investigation. We are indebted to Berthier*, Dumas†, Gras‡, and lately Peligot, for an analysis of this substance. The glass analysed by these chemists was of the kind usually employed in the manufacture of Bohemian goblets, an art in which Bohemia has excelled for centuries.

It appeared desirable to compare with the results of these analyses the composition of the glass which is used for the combustion of organic substances, and which likewise is chiefly manufactured in Bohemia. The properties most valued in this variety of glass are essentially different from those sought for in other kinds, and it was to be expected that this material, which has so greatly contributed to the progress of organic chemistry, and upon which the German manufacturers have of late bestowed so much attention, would also show some marked peculiarity of composition.

The following analysis was made in the laboratory of the Royal College of Chemistry. The glass was selected from the stock of the laboratory, recently imported from Germany, and which numerous trials had proved to be of first-rate quality. The tubes, though perfectly tractable in an energetic blowpipe flame, scarcely altered their form during the longest combustion in a strong charcoal fire; they never cracked during the process, even on suddenly increasing the temperature, and not uncommonly the same tube could be employed repeatedly in analysis.

A careful qualitative examination of the specimen having proved the presence of silicic acid, lime, sesquioxide of iron, alumina, oxide of manganese, magnesia, soda and potassa, the quantitative determination was proceeded with.

### *a. Determination of Silicic Acid.*

The finely-powdered glass was ignited with carbonate of soda, treated with hydrochloric acid in excess, evaporated to dryness, once more ignited and digested with hydrochloric acid, after which all the silicic acid remained insoluble; it was collected on a filter, washed, ignited and weighed.

I. 2·1890 grms. of glass gave 1·5946 grm. silicic acid.

II. 2·1284 grms. of glass gave 1·5628 grm. silicic acid.

* Gmelin's *Handbuch*, vol. ii. 366.

† Dumas' *Traité de Chemie*, vol. ii. 528. ‡ *Ibid.*

*b. Determination of Lime.*

The acid filtrate from the silicic acid was neutralized by ammonia, then slightly acidulated with acetic acid and precipitated by oxalate of ammonia, and the oxalate of lime converted into carbonate in the usual manner.

I. 2·1890 grms. of glass gave 0·4203 grm. of carbonate of lime.

II. 2·1284 grms. of glass gave 0·3843 grm. of carbonate of lime.

*c. Determination of Alumina and Sesquioxide of Iron.*

To the liquid filtered from the precipitate of oxalate of lime (*b.*), containing a large quantity of chloride of ammonium, ammonia was added in excess, by which alumina and sesquioxide of iron were precipitated and the oxide of manganese and magnesia were retained in solution. The joint precipitate of alumina and sesquioxide of iron was collected, washed, ignited and weighed; then dissolved in hydrochloric acid and thrown down with potassa, which kept the alumina in solution. The precipitate of sesquioxide of iron (thus obtained), once more dissolved in hydrochloric acid and reprecipitated by ammonia, was now collected, ignited and weighed; the difference in the amount of the two weighings gave the amount of the alumina thus:—

2·1890 grms. of glass gave 0·0096 grm. of mixed oxides and 0·0029 grm. of sesquioxide of iron; the difference, 0·0067 grm., is the amount of alumina.

*d. Determination of Oxide of Manganese.*

This oxide was thrown down by carbonate of soda as carbonate of manganese, from the filtrate, separated from the oxide of iron and alumina (*c.*); the precipitate was washed, dried, ignited, and calculated as the compound oxide and sesquioxide of manganese ($Mn_3 O_4$).

I. 2·1890 grms. of glass gave 0·0114 grm. of the above-named double oxide.

II. 2·1284 grms. of glass gave 0·0160 grm. of the double oxide.

*e. Determination of the Magnesia.*

The filtrate from the carbonate of manganese (*d.*) was precipitated by phosphate of soda; the phosphate of magnesia and ammonia was washed, dried, ignited and weighed as pyrophosphate of magnesia.

I. 2·1890 grms. of glass gave 0·0127 grm. of pyrophosphate of magnesia.

II. 2·1284 grms of glass gave 0·0177 grm. of pyrophosphate of magnesia.

### *f. Determination of the Alkalies.*

To determine the amount of the alkalies, a portion of the glass was fused with hydrate of baryta; the fused mass was digested in hydrochloric acid, evaporated to dryness and ignited, the residue again digested in hydrochloric acid, and then filtered from the insoluble silicic acid. Carbonate of ammonia was then added to the filtrate, to separate the alumina, sesquioxide of iron, baryta and lime; the solution filtered from the precipitate was evaporated to dryness and ignited, to drive off the ammoniacal salts, and the magnesia separated by means of baryta; the excess of baryta was separated by means of carbonate of ammonia, and filtered. The filtrate, evaporated to dryness and ignited, yielded the mixed chlorides of the alkaline metals; they were dissolved in water, bichloride of platinum added, and the solution evaporated to dryness on a water-bath; the residue was digested in strong alcohol, when the potassio-chloride of platinum remained undissolved; it was collected on a weighed filter, washed with alcohol, and dried in a water-bath until it ceased to lose weight. The filtrate from the potassio-chloride of platinum was evaporated to dryness, and, after the addition of some oxalic acid to the residue, ignited till it was completely decomposed; the residue was digested in water, filtered, and the filtrate evaporated to dryness in a weighed capsule; its increase in weight gave the quantity of chloride of sodium.

1·5645 grm. of glass gave 0·9330 grm. of potassio-chloride of platinum, and 0·0905 grm. of chloride of sodium.

From the results enumerated, the calculated per-centage is as follows:—

| | I. | II. | Mean. |
|---|---|---|---|
| Silica . . . . . | 72·84 | 73·42 | 73·13 |
| Lime . . . . . | 10·75 | 10·11 | 10·43 |
| Alumina . . . . . | 0·30 | ... | 0·30 |
| Peroxide of iron . . . | 0·13 | ... | 0·13 |
| Magnesia . . . . . | 0·21 | 0·30 | 0·26 |
| Protoxide of manganese | 0·37 | 0·54 | 0·46 |
| Soda . . . . . | 3·07 | ... | 3·07 |
| Potash . . . . . | 11·49 | ... | 11·49 |
| | 99·16 | | 99·27 |

The amount of oxygen in the bases stands to the amount of oxygen in the silicic acid nearly as 1 : 6.

From the preceding analysis, it results that the composition of the glass for combustion-tubes does not differ very much

from the material employed in goblets, as may be seen from the following comparison with the results of the chemists formerly named:—

| | Berthier. | Dumas. | Gras. | Peligot. |
|---|---|---|---|---|
| Silicic acid . . . | 71·7 | 69·4 | 71·6 | 76 |
| Lime . . . . . | 10·3 | 9·2 | 10·0 | 8 |
| Alumina . . . . . | 0·4 | 9·6 | 2·2 | 1 |
| Sesquioxide of iron . | 0·3 | ... | 3·9 | |
| Oxide of manganese | 0·2 | ... | 0·2 | |
| Magnesia . . . . . | ... | ... | 2·3 | |
| Soda . . . . . | 2·5 | ... | ... | |
| Potassa . . . . . | 12·7 | 11·8 | 11·0 | 15 |
| | 98·1 | 100·0 | 101·2 | 100 |

In one of the last numbers of Dr. Otto's German translation of Professor Graham's Elements of Chemistry, recently published, I find the analysis of a combustion-tube enumerated, performed in the laboratory of Dr. Otto, which has not yet been published in the Journals. He obtained the following results:—

| | |
|---|---|
| Silicic acid . . . . . | 74·0 |
| Lime . . . . . | 7·2 |
| Alumina . . . . . } | 0·1 |
| Sesquioxide of iron . } | |
| Potassa . . . . . | 18·5 |
| | 100·0 |

The oxygen in the bases of this glass stands to the oxygen in the silicic acid likewise as 1 : 6. Soda is entirely absent, and completely replaced by potassa. The presence however of a small amount of soda does not seem to be injurious to the glass.

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January 4, 1847.—James Lowe Wheeler, Esq. in the Chair.

A Memoir on Picoline, by Dr. T. Anderson, was presented from the author.

Messrs. Dugald Campbell and Benjamin H. Paull were elected Members of the Society.

The following papers were read:—

Note on the Preparation of a fixed Manure from Urine. By Dr. Robert Angus Smith.

As a practical point in the management of this manure I think the following useful. I added some carbonate of magnesia to urine and found in about twelve hours crystals of phosphate of magnesia and ammonia. This is probably the only insoluble salt of ammonia which we can expect to get from the chemical manipulation of urine; it is also one in which the most valuable portions of the manure are

preserved. There is no loss of room from the presence of useless materials, and it is therefore well-suited for transportation. The crystals are large and distinct, and can easily be separated from the liquid. The natural carbonate acts too slowly I fear to be recommended. I tried the magnesian limestone, but did not get good results on a small scale. But if acid is added, or if sulphate of magnesia be used, the results are as rapid as with the fine precipitated carbonate of magnesia.

It is true, that if acid be added to the magnesian limestone the lime also must be supplied and more acid be wanted, but I think the price of sulphuric or muriatic acid and the price of sulphate of magnesia are sufficiently low to make the plan of value in many districts: in towns no doubt it could be easily managed. It will be advisable to choose such limestone as contains about an equivalent of magnesia.

## CLXXXVII. *On Thialdine and Selenaldine, two new artificial organic bases. By* Wöhler *and* Liebig. *Communicated by* Dr. A. W. Hofmann.

### 1. *Thialdine.*

THE peculiar deportment of hydrated cyanic acid with aldehyde, which gives rise to a new acid containing the elements of aldehydite of ammonia and hydrated cyanic acid, induced us to study the action of some other substances on aldehyde and aldehydite of ammonia.

The most interesting product which we obtained along with others, is a new organic alkali free from oxygen, and containing carbon and hydrogen in the same proportions as acetic acid, combined with sulphur and the elements of sulphide of ammonium. This substance, which we call thialdine*, is highly remarkable from its composition, and we have no doubt that the method which led to its discovery, when applied to other compounds analogous to aldehyde and aldehydite of ammonia, will yield a long series of new and interesting products. The study of these substances promises to become highly important for the theory of the formation of organic bases, in which the action of ammonia is frequently very prominent, and it may be expected that a close investigation of the production of organic substances containing sulphur will throw some light upon their generation in the organism of the plant.

The preparation of thialdine is very simple. One part of aldehydite of ammonia free from æther and alcohol is dissolved in from twelve to sixteen parts of water; one ounce of this liquid is mixed with from ten to fifteen drops of solution

* Contracted from θεῖον and aldehyde.

of ammonia, and treated with a slow stream of hydrosulphuric acid; after half an hour the solution begins to become turbid, and crystals are deposited of the appearance of camphor and of considerable size; after four or five hours the liquid again becomes clear and the operation is terminated. The crystals are collected on a funnel and washed with water until all the sulphide of ammonium is separated. Pressure between bibulous paper removes the adhering water. The dry crystals are dissolved in æther, the solution mixed with a third of its volume of alcohol and left to spontaneous evaporation. The liquid soon deposits very regular rhombic tables, which can be obtained of half an inch in dimensions if too rapid an evaporation of the solution has been avoided.

If no more of the solution is left than is required to cover the crystals formed, the mother-liquid is decanted off; the crystals are then dried by leaving them for some time between folds of bibulous paper. The mother-liquor yields some more thialdine on evaporation. The crystals thus obtained are however not quite colourless. The remaining liquid contains much sulphide of ammonium, part of which arises from the ammonia added.

It happens sometimes that on passing hydrosulphuric acid gas through the solution of aldehydite of ammonia, no crystalline body, but a heavy colourless oil of offensive odour is deposited. This oil is a mixture of two bodies, the greater part being thialdine, the fusing-point of which is depressed to the temperature of the atmosphere by the presence of a liquid substance*. In order to obtain pure thialdine from this mixture, the supernatant aqueous layer is separated, and the remaining liquid (consisting principally of the oil and but a small amount of the aqueous solution) is agitated with half its bulk of æther, which instantaneously dissolves the oil. The æthereal solution, which may be easily separated from the water, is agitated in a stoppered bottle with a little concentrated hydrochloric acid. The mixture generally solidifies as a mass of fine needles, which may be separated from the oil by washing with æther. In this manner hydrochlorate of thialdine is obtained, from which pure thialdine may easily be prepared by moistening the dry crystals with a concentrated solution of ammonia, and extracting the separated base by means of æther. The æthereal solution yields by spontaneous evaporation crystals of pure thialdine. Addition of alcohol to the æthereal solution facilitates the crystallization

* Crystals of thialdine when placed in contact with sulphide of ammonium for some time are entirely converted into a heavy oil, insoluble in water, which has not been further examined.

exceedingly; the crystals become larger, more regular, and perfectly transparent.

Pure thialdine is heavier than water; its specific gravity is 1·191 at 18° C.; it forms large, transparent, colourless, shining crystals of the form of common gypsum, possessing a highly refracting power and a peculiar aromatic, but after some time very disagreeable odour. The crystals fuse at 43° C.; the fused crystals solidify at 42°; they are volatile at the temperature of the atmosphere without residue. Thialdine distils with the vapour of water, but is decomposed when distilled alone, a heavy oil of offensive odour passes over, solidifying only partly and after some time, whilst a brown, syrupy residue containing sulphur is left in the retort. Thialdine in this respect resembles aldehydite of ammonia, which, though volatile itself, cannot be exposed to a higher temperature without decomposition. If a crystal of thialdine remains for several hours in an atmosphere containing acid vapours, such as is the case in the laboratory, a white envelope of fine silky needles is found at a certain distance from the planes of the crystals.

Thialdine is but little soluble in water; it is soluble in alcohol, and much more so in æther; when powdered it deliquesces at the common temperature in vapour of æther, or in an atmosphere containing vapour of æther.

An alcoholic solution of thialdine exhibits the following reactions:—

With acetate of lead, at first no precipitate, but after some time a yellow deposit appears, which soon becomes red and finally black.

Nitrate of silver causes a precipitate, which at first is white, then yellow, afterwards black.

With chloride of mercury a white precipitate is produced, turning rapidly yellow.

With bichloride of platinum a dingy, yellow precipitate is thrown down after some time.

Thialdine has no reaction on vegetable colours; it is soluble in all acids with which it combines, forming crystallizable salts; the hydrochlorate and the nitrate are remarkable for the facility with which they crystallize and for the beauty of the crystals.

Thialdine and its salts are decomposed when gently heated with a solution of nitrate of silver; sulphide of silver is produced with disengagement of a combustible gas, easily inflammable and possessing the odour and all the properties of aldehyde; namely, it is entirely absorbed by concentrated sulphuric acid and solution of potassa, the former becoming

brown immediately, the latter remaining clear but depositing when gently heated a yellowish-brown precipitate of resin of aldehyde, and assuming the peculiar and offensive odour which accompanies the decomposition of aldehyde under these circumstances.

When thialdine is ignited with lime, chinoline appears among the products of decomposition, which may be easily recognised by its characteristic odour and by its beautiful platinum salt.

With cyanide of mercury thialdine exhibits a peculiar comportment. On mixing the two solutions a white precipitate is produced, which on boiling is converted into amorphous, black sulphide of mercury. If this decomposition takes place in a retort its neck becomes coated with fine crystalline needles, extremely volatile, insoluble in water but easily soluble in alcohol and æther. This new body, in which part or all the sulphur appears to be replaced by cyanogen, is formed in but small quantities, which up to this moment has prevented us from studying it any further.

The analysis of thialdine was performed in the usual way; the combustion with oxide of copper is attended with difficulties, as the conversion of carbon into carbonic acid is obstructed by the large quantity of sulphur contained in the body forming a corresponding amount of sulphide of copper at the point of contact between the substance and oxide of copper.

On burning thialdine with oxide of copper and separating the sulphurous acid formed by means of peroxide of lead, a gas is obtained containing volumes of nitrogen and carbonic acid in the proportion of 1 : 12. Aldehydite of ammonia, from which thialdine is produced, contains 4 equivs. of carbon to 1 equiv. of nitrogen, from which it is evident that aldehydite of ammonia on being converted into thialdine by means of hydrosulphuric acid has lost two-thirds of its nitrogen.

We have mentioned that thialdine, on being gently heated with a solution of nitrate of silver, has its sulphur converted into sulphide of silver. This mode of decomposition was employed to determine the sulphur. The nitrogen of the thialdine remains in the residuary liquid in the form of ammonia, from which it was precipitated by bichloride of platinum, and determined in the usual way*.

0·3633 grm. of thialdine gave 0·5845 grm. of carbonic acid and 0·267 grm. of water.

* The following analyses were made by Dr. Strecker at Giessen, and Dr. Städler in Göttingen.

0·509 grm. of thialdine gave 0·816 grm. of carbonic acid and 0·3720 of water.

0·4508 grm. of thialdine gave 0·566 grm. of ammonio-chloride of platinum.

0·6430 grm. of thialdine gave 1·923 grm. of sulphide of silver.

0·3140 grm. of thialdine gave 0·8420 grm. of water.

The atomic weight having been ascertained by the analysis of the hydrochlorate and nitrate, the preceding numbers lead to the following formula—

$$C_{12}\ H_{13}\ N\ S_4,$$

as will be seen on comparing the theoretical and experimental numbers.

| | | | | Theory. | Mean of experiments. |
|---|---|---|---|---|---|
| 12 | eqs. of | Carbon . . | 72 | 44·17 | 43·80 |
| 13 | ... | Hydrogen . | 13 | 8·04 | 8·04 |
| 1 | ... | Nitrogen . . | 14 | 8·58 | 8·54* |
| 4 | ... | Sulphur . . | 64 | 39·26 | 39·14 |
| | | | 163 | | |

*Hydrochlorate of Thialdine.*—Thialdine is dissolved in large quantity by hydrochloric acid: the saturated solution has an acid reaction. On spontaneous evaporation, or concentration on the water-bath, it deposits large, regular, transparent prisms of great lustre, and frequently an inch in length. The hydrochloric solution of crude thialdine contains in admixture a foreign body of most offensive odour; on agitating with æther this odour disappears immediately, and the liquid which formerly was turbid becomes perfectly transparent. Hydrochlorate of thialdine is rather soluble in water, less so in alcohol; both liquids dissolve a large quantity when hot, and deposit beautiful and perfectly regular crystals on cooling. Hydrochlorate of thialdine is insoluble in æther. When heated in the dry state this salt is decomposed without fusion; it becomes brown, and chloride of ammonium sublimes with evolution of a gas possessing a most offensive odour and burning with a dull flame. From the solution of this salt nitrate of silver throws down a yellow precipitate, which, on being gently heated, turns black with evolution of aldehyde. This black precipitate is a mixture of chloride and sulphide of silver; all the nitrogen of the base remains in the liquid in the form of ammonia.

0·4577 grm. of hydrochlorate of thialdine gave 0·5933 grm. of carbonic acid and 0·2850 grm. of water, corresponding to 35·35 per cent. of carbon and 6·92 per cent. of hydrogen.

* Calculated from the proportion of 12 C : 1 N.

0·726 grm. of hydrochlorate of thialdine gave 0·789 grm. of ammonio-chloride of platinum.

0·7735 grm. of hydrochlorate of thialdine gave 0·8225 grm. of ammonio-chloride of platinum. In the mean, 6·79 per cent. of nitrogen.

0·7798 grm. of hydrochlorate of thialdine gave 1·890 grm. of sulphide of silver = 32·09 per cent. of sulphur.

0·7735 grm. of hydrochlorate of thialdine gave 1·915 grm. of sulphide of silver = 31·92 per cent. of sulphur.

0·7598 grm. of hydrochlorate of thialdine was precipitated with nitrate of silver and boiled until evolution of gas had ceased; the precipitate, when extracted with ammonia and precipitated with nitric acid, gave 0·5283 grm. of chloride of silver = 17·14 per cent. of chlorine.

0·7735 grm. treated in the same way, gave 0·5405 grm. of chloride of silver = 17·24 per cent. of chlorine.

0·776 grm. dissolved in alcohol and precipitated in the same manner with nitrate of silver, gave 1·912 grm. of sulphide of silver = 31·903 per cent. of sulphur and 0·551 grm. of chloride of silver = 17·551 per cent. of chlorine.

0·441 grm. ignited with a mixture of lime and nitrate of potassa, gave 0·32 grm. of chloride of silver = 17·94 per cent. of chlorine.

These results lead to the following formula for hydrochlorate of thialdine,—

$$C_{12}H_{13}NS_4, HCl,$$

as may be seen from the following comparison between the theoretical and experimental numbers:—

| | | | | Theory. | Mean. |
|---|---|---|---|---|---|
| 12 | eqs. of | Carbon . . | 72 | 36·10 | 35·35 |
| 14 | ... | Hydrogen . | 14 | 7·02 | 6·79 |
| 1 | ... | Nitrogen . | 14 | 7·02 | 6·92 |
| 4 | ... | Sulphur . . | 64 | 32·09 | 31·97 |
| 1 | ... | Chlorine . | 35·4 | 17·77 | 17·47 |
| | | | 199·4 | 100·00 | |

*Nitrate of Thialdine.*—This salt may be obtained by mixing this base directly with dilute nitric acid; it is, however, preferable to dissolve crude thialdine in æther, and agitate the liquid with moderately concentrated nitric acid; the solution solidifies into a crystalline mass, which is washed with æther, dissolved in water, and crystallized by evaporation and cooling.

Nitrate of thialdine forms fine white needles, more soluble in water than the hydrochlorate; they are soluble in cold, and more so in hot alcohol, from which liquid they likewise recrystallize on cooling: they are insoluble in æther; on heating they fuse and are decomposed.

On burning this salt with chromate of lead, more accurate numbers for the carbon and hydrogen were obtained than in the analysis of thialdine itself or the hydrochlorate, a result which can easily be explained by the co-operation of the oxygen in the nitric acid.

0·357 grm. of nitrate of thialdine gave 0·4155 grm. of carbonic acid and 0·2045 grm. of water.

0·514 grm. of nitrate of thialdine gave 1·116 grm. of sulphide of silver.

0·6696 grm. of nitrate of thialdine, when ignited with a mixture of potassa and nitre, gave 1·4063 grm. of sulphate of baryta; the mean of the two latter experiments equals 28·4 per cent. of sulphur.

These results lead to the following formula for nitrate of thialdine,— $C_{12}H_{13}NS_4, HNO_6$,

as will be seen by the following comparison between the theoretical and experimental numbers:—

| | | | Theory. | Experiment. |
|---|---|---|---|---|
| 12 eqs. of | Carbon | 72 | 31·80 | 31·75 |
| 14 ... | Hydrogen | 14 | 6·19 | 6·36 |
| 2 ... | Nitrogen | 28 | | |
| 4 ... | Sulphur | 64 | 28·34 | 28·40 |
| 6 ... | Oxygen | 48 | | |
| | | 226 | | |

The formation of thialdine is easily accounted for: 3 eqs. of aldehydite of ammonia and 6 eqs. of hydrosulphuric acid transpose into 1 eq. of thialdine, 6 eqs. of water, and 2 eqs. of sulphide of ammonium.

| | |
|---|---|
| 3 eqs. of Aldehydite of ammonia . | $C_{12}H_{21}N_3O_6$ |
| 6 ... of Hydrosulphuric acid . . | $H_6S_6$ |
| | $C_{12}H_{27}N_3S_6O_6$ |
| 1 eq. of Thialdine . . . . . | $C_{12}H_{13}NS_4$ |
| 6 eqs. of Water . . . . . | $H_6O_6$ |
| 2 ... of Sulphide of ammonium . | $H_8N_2S_2$ |
| | $C_{12}H_{27}N_3S_6O_6$ |

But the question respecting the real constitution of this body is too closely connected with that of the true constitution of organic bases in general to admit of any definite opinion being promulgated at this moment, when so few experiments on the subject are as yet before us. Still we can imagine how important for the general question facts like the formation of thialdine may hereafter become, and that just from this quarter perhaps a way for its solution may be obtained. We will here merely allude to an explanation of the

constitution and basic character of thialdine, at once obvious, namely, that it may be regarded as a copulated compound of sulphide of ammonium with 3 eqs. of a body

$$C_4 H_3 S,$$

which is the sulphide corresponding to the oxide in aldehyde, namely, sulphide of acetyl.

### 2. *Selenaldine.*

The existence of thialdine and the mode in which this base is formed, induced us to try the preparation of a corresponding selenium compound. We perfectly succeeded in obtaining that body: selenaldine, however, is so soon and easily altered, that we have not as yet been able to subject it to a more profound investigation.

Selenaldine was produced by passing into a concentrated solution of aldehydite of ammonia hydroselenic acid gas, disengaged from selenide of iron by means of sulphuric acid. In order to prevent the decomposition of hydroselenic acid by the oxygen of the atmosphere, the whole apparatus had been filled previously with hydrogen. The excess of the poisonous hydroselenic acid was condensed in a potassa apparatus. After some time the solution of aldehydite of ammonia begins to become turbid, and crystals of selenaldine are deposited. When the mass of crystals is no longer augmented, the excess of hydroselenic acid is expelled by a stream of hydrogen gas; the solution of selenide of ammonium, covering the crystals, which soon turns red and deposits selenium, is now displaced by introducing a stream of cold water, free from atmospheric air, through one of the glass tubes connected with the bottle. The crystals are then collected upon a filter, pressed between folds of bibulous paper and dried over sulphuric acid.

Selenaldine, as it is deposited from the liquid in which it forms, presents itself in small colourless crystals, doubtless isomorphous with thialdine. In contact with the atmosphere it turns immediately yellow. This substance has a feeble but disagreeable odour; it is slightly soluble in water, on which account it should not be washed too long. The aqueous solution and the last washings become soon turbid in contact with the atmosphere, and deposit an orange-yellow body. The same deportment is exhibited by the solution of selenaldine in alcohol and æther, in both of which it is easily soluble. In consequence of its being so easily altered, we did not succeed in obtaining this base in crystals from any of the solutions mentioned. On evaporating them *in vacuo* over

sulphuric acid, the greater portion of the substance is volatilized with decomposition, the yellow body being likewise produced, while sulphate of ammonia is formed in the sulphuric acid. Also, when heated alone, selenaldine is decomposed, with disengagement of a gas of most offensive odour. Selenaldine is a base like thialdine; it is soluble in dilute hydrochloric acid, and reprecipitated by ammonia as a crystalline mass. The hydrochloric solution also immediately decomposes with evolution of a most offensive odour. Selenaldine is altered in a similar manner by boiling with water. The yellow body, the formation of which seems to be always attended with a liberation of aldehydite of ammonia, when collected is orange-yellow, amorphous, soluble in alcohol and æther, and fuses, when heated with water, to a reddish yellow mass, which remains soft for a long time. When heated alone, this body is charred with evolution of an oil containing selenium and possessing a most offensive odour.

We did not obtain a decisive result when trying to produce a *telluraldine*, the tellurium which we employed in the preparation of the hydrotelluric acid accidentally containing so large an amount of selenium, that merely selenaldine was deposited from the purple solution, containing, as it appeared, only telluride of ammonium. We intend to repeat this experiment with tellurium free from selenium.

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## CLXXXVIII. *Some Remarks on the Air and Water of Towns.* By Robert Angus Smith, *Ph.D.*

HAVING given considerable attention to the inquiry into the causes affecting the health of towns, I was anxious to find what the real evil in their polluted atmosphere consisted of; the air has been frequently examined, but the differences found do not sufficiently account for the differences perceptible in breathing for the first time in entering a large town from the country, or for the very great difference in the colour and appearance of both when contrasted side by side, by an individual outside a town, having both before his eyes. The accumulation is great in this case, it is true, but therefore so much the more fitted for showing us its true character.

I first examined the rain-water taken from a cistern; a little was boiled down and the solid residue was like fatty matter, which burnt and gave the smell of a fat, leaving afterwards a strong odour of nitrogenized organic matter. As this amounted to nearly one per cent., I was disposed to con-

sider it an accidental impurity, and collected some rain in a porcelain vessel previously carefully cleaned. A smaller amount was obtained, but still from 500 grains of the water a sufficient quantity to make the smell distinct. I know that organic matter has been found in rain-water, but I am not aware that the smell of nitrogenized matter has been distinctly observed. It has been obtained also by boiling down large quantities: I have never found it to fail in evaporating as little as 1000 grs. The amount was generally about ·01 of a grain in 1000 grs., but the average cannot be got without trying many seasons and many places.

1000 grs. collected on the 23rd of November, 1846, in a platinum vessel, after raining thirty hours with little intermission, gave with nitrate of silver a precipitate weighing 0·11 grs. = 0·027 of chlorine, and with a salt of barytes 0·1, equal to 0·0343 grs. of sulphuric acid, besides a perceptible smell of organic matter as before.

I do not adduce this analysis as of any great importance in showing the amount; the quantity operated upon is small, and I was desirous, for the sake of the salts, not to expose it to the contact of any vessel which could be acted on; but I mention it to show, that the quantity is not such as can be only procured by the questionable process of boiling down large quantities in vessels too large to admit of being perfectly cleaned.

The water is often alkaline—I say often, but I have always found it so; by boiling this is lost, proving, as I think, that there is more carbonate of ammonia set free from the burning of coals than is necessary to saturate the sulphuric acid in the atmosphere.

The air is often acid, as evidenced by test-papers exposed to it; and it certainly proves very acid when certain quantities of coal are burnt.

It would have been well to have examined water from the country falling at the same time, but being persuaded that water so impure would long ago have been examined if it even fell over large districts in such a state, I preferred looking to its origin.

As far as I am aware no examination of unventilated places has given us a good proof that carbonic acid is the greatest agent in making them so actively injurious. I breathed, and had others to breathe, through a bent tube into a large jar, and examined the moisture in the jar. As it always contained organic matter in large quantities, I inferred that the same must occur when the perspiration and breath condense upon the windows of crowded rooms.

This condensed moisture is not easily obtained in sufficient quantities; but on the occasion of a concert at the Mechanics' Institution here, I collected 200 grs. from one window, letting it drop into a small platinum basin. By burning 5 grs. of this the smell was made apparent; by burning 150 grs. a strong smell of human sweat came off, continuing until the substance was dry. It will therefore be difficult to tell how much organic matter was contained in the whole, as a great deal evaporated, but above 2 grs. were left. When heated, this smelt like burning flesh, and was very disagreeable.

We know that volatile products escape from the bodies of animals, and are mixed with the air so as to undergo complete oxidation; but this cannot be any important part which the air has to perform, as the following facts show that the oxidation is best effected in the earth. It may however be important that bodies should decompose in this manner, because they are also more readily conveyed by the atmosphere to plants.

When we see the volatile and decomposing matter from the body so distinctly as in the last case mentioned, it is possible for us to conceive that infectious matter is not a substance so very subtle as has been supposed; we have only to allow it to be in a peculiar state of decomposition.

Burning in a platinum crucible and the odour discover a very small quantity of organic matter, such as it is scarcely safe to trust to the results of the balance. I hope in a future paper to show the qualities of several water districts in this respect, but at present give an abstract only of the results of such observations as I have made, hoping that the constant and almost monthly variation of the water of whole districts will be a sufficient excuse for the absence of an arranged set of results.

When water from a peaty district is boiled down and the ashes burnt, the smell of peat is distinctly observed. The river Dee at Chester contains 25 grs. of organic matter to the gallon, and the smell is as perceptible as at Llangollen, close to a peaty district. 500 grs. of the water are sufficient to indicate this very strongly. Water from the Lancashire and Yorkshire hills may be known to contain peat also by testing the same quantity, although many of the streams do not contain 15 grs. per gallon. Some of the canals near Manchester may be known to be supplied from peaty districts by the same tests. But whenever we approach a town the smell from the burnt ash changes, and organic matter from the decomposition of protein compounds is distinctly traced. So easily is this known, that when water was brought to me

from the Dee, above Llangollen and below, it appeared evident that even this small town had affected the river. Before the water arrives at Chester the peat predominates too much to make it perceptible that matter from towns has been thrown into it; below it is distinct. Water from surface-drainage indicates by the same mode of treatment nitrogenous matter undecomposed.

Observing this increase of organic matter on approaching towns, I naturally expected to find a large quantity in the wells, of which there are many in Manchester, placed as they often are in the neighbourhood of cesspools, besides being exposed to the infiltration of the water of drains.

A well was first examined in a garden near the town, the proprietor having complained of it as being unwholesome. It contained 40 grs. of common salt per gallon, 14 grs. of organic matter and salts of ammonia, besides other ingredients to be expected in connection with organic matter. I next examined a well near a burying-ground; it was loaded with inorganic salts. Its taste was very bitter; when evaporated and burnt, the remaining inorganic matter gave out a pungent acid vapour. Four wells in the same neighbourhood were examined, all with the same results. I then went to nearly all the churchyards in Manchester, of which there is a considerable number, but finding that the neighbourhood of the collegiate church gave the same indications as all the rest, although there have been no burials there for many years, I was induced to ascribe it to the presence of large dung-heaps close to the well. Other wells distant from churchyards, but near cesspools, gave the same result. In the suburbs they were not so much tainted, but in some newly-built streets close to the town, in gravelly soil, were very bad.

I have no doubt that the churchyards and the cesspools act in a similar manner, as we might naturally expect. The chief impurity is a collection of inorganic salts. It is remarkable how rapidly the organic matter becomes oxidized and converted into nitric acid in the soil. In one case I found as much as 70 grs. of nitrates in a gallon of water, besides magnesia, lime and alkalies. This water seems to be a favourite with some persons; when not quite so heavily charged it has a fine sparkling appearance. The wells in the centre of the town have nearly disappeared, otherwise it is probable that organic matter would have been found there in a less oxidized state.

As these wells have undergone several changes during the autumn and early part of the winter, I shall not give the results of the analyses which I have made, until a few seasons shall enable me to make a more complete examination of the

subject. At present, when the ground is so wet, it is difficult to obtain a sufficient quantity of the salts, which are peculiar. At present I may say that sulphuric acid added to the water gives off chlorine; that heat evolves chlorine and peroxide of nitrogen from it; and that the remaining salt is a mixture of a chloride and a nitrate chiefly. This will be sufficient to show that neither the water nor the air of Manchester has so very minute an amount of impurity as to put it without the power of detection.

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January 18, 1847.—John Thomas Cooper, Esq., Vice-President, in the Chair.

Messrs. John Mercer, Jun., A. F. Gatty, and R. Dugdale Kay, were elected Members.

Note on the Action of a Solution of Caustic Soda upon a Stoneware Jar. By Mr. Trenham Reeks.

Having been puzzled in the analyses of some bronzes and iron ores, with the presence of an excessive quantity of alumina, I was induced to examine the reagents employed, and found that this excess originated in the soda, which had for some time been standing in an earthenware jar. I send a piece of this jar which exhibits a thick coating, nearly all composed of silica, the alumina having been dissolved out by the soda.

On some improved Forms of Chemical Apparatus. By Thomas Taylor, Esq.

Among the many advantages possessed by the Chemical Society, it appears to me not the least, that it affords to its members a ready mode of communicating to one another many of those little practical facts and modes of operating, which, although perhaps not of sufficient importance to merit distinct notice in the scientific journals, are nevertheless of considerable value to those engaged in the prosecution of the science. In furtherance of this view I will therefore describe some new forms of apparatus which I have myself been in the habit of using for some time past.

The first of these is a mode of closing the mouths of gas-bottles, or indeed of any wide-mouthed vessel into which tubes are to pass, as in Woolf's apparatus, gas generators, &c. To effect this the top of the bottle is first to be slightly ground, so as to procure a level surface, a piece of sheet caoutchouc is then laid upon it, and this is covered by a disc of wood of the same size as the top of the bottle, and from a quarter to half an inch in thickness. The wooden cover is held in its place by means of a small double clamp of brass or of varnished sheet iron, which passes across the cover, and the ends of which are bent under the rim of the bottle, against which they are pressed by a screw fixed in the centre of the clamp. By turning the screw the caoutchouc is sufficiently compressed to render the joint perfectly air-tight. The tubes intended to pass into and out

of the bottle are cemented into the wooden cover, usually on one side of the clamp; and they pass of course through corresponding holes in the caoutchouc. By making these holes somewhat smaller than the diameter of the tubes, the caoutchouc contracts so closely around them, that not only is any liquid which might be accidentally thrown up effectually prevented from getting between the caoutchouc and the wooden cover, but the necessity of cementing the tube into the cover may be even dispensed with. This method is so effectual and easily arranged, that I am quite convinced it will supersede the use of corks in the preparation of all gases which only require the application of a moderate heat and do not act upon caoutchouc. Ground glass plates might of course be substituted where caoutchouc is inapplicable, or a sheet of ground glass might be cemented upon the lower part of the wooden cover; but these modes would be rather expensive, and the cases in which they would be required are not very numerous. In small bottles the use of a clamp is not essential, as sufficient pressure may be obtained by inserting two wedges of wood beneath a string tied around the neck, and over the top of the bottle.

Fig. 1.

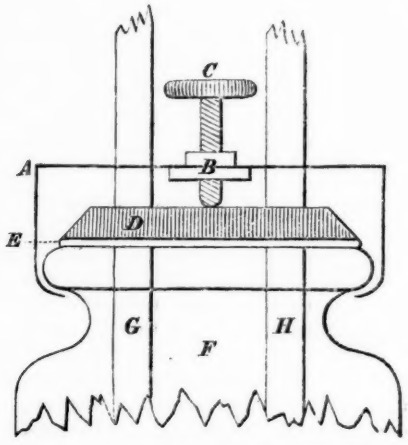



Fig. 1. A clamp of sheet iron having a small centre of brass B, in which the screw C works. D disc of wood. E sheet of caoutchouc. F glass bottle. G H glass tubes.

I will next direct the attention of the Members to a new mode of cupelling, or rather to a new form of muffle. Cupellation is an operation not often performed by amateurs, chiefly I believe on account of the difficulty in doing it unless provided with furnaces built expressly for the purpose. The following plan I have found to afford most accurate results, while it may be performed in almost any furnace:—The mouths of two black lead crucibles of the same size are to be ground flat, so that when applied one to the other they may stand quite steady. An oblong or semicircular notch is to be cut out of the mouth of one of the crucibles, and a hole is also to be

drilled through its bottom. This crucible when placed upon the top of the other constitutes the muffle, and of course resembles in shape a skittle. To cupel with this apparatus, the lower crucible is nearly filled with clean sand, set upon the bars of the grate in the centre of the furnace, and brought to a low red heat. The cupel containing the lead and the alloy is then placed upon the sand and immediately covered by the other crucible, taking care that the notch in its side shall be opposite to, and correspond with the furnace-door; more fuel is added, during which it is well to cover the hole in the top of the muffle with a crucible lid, in order to prevent the admission of dirt. When the muffle has become throughout of a bright red heat, the furnace-door is thrown open, and the ignited fuel gently moved aside, so as to permit a view of the side opening in the muffle. The current of air which is thus established through the muffle instantly causes rapid oxidation of the lead, and this may be regulated at pleasure by closing the door more or less. If from the fuel falling down any difficulty should be experienced in maintaining a free passage for the air, a portion of a porcelain tube or a gun-barrel may be passed through the furnace-door to within an inch of the muffle; but this proceeding is generally rendered quite unnecessary by taking care to place some large pieces of coke immediately around the door of the furnace.

In many cases it will be found advantageous to convert the lower crucible itself into the cupel by first half-filling it with sand and then ramming in pounded bone-earth. I have found the above method to possess the following advantages:—In the first place, the crucibles may be maintained at a much higher temperature than can be readily obtained when the ordinary muffle is used, while the degree of heat and the quantity of air admitted may be regulated with the greatest nicety. Secondly, owing to the greater draught of air, the oxidation of the lead is more quickly effected; and lastly, by looking through an opening in the furnace cover, the operation may be watched from first to last.

Fig. 2.

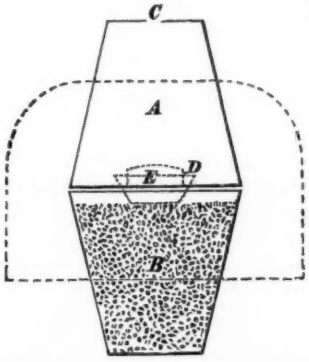
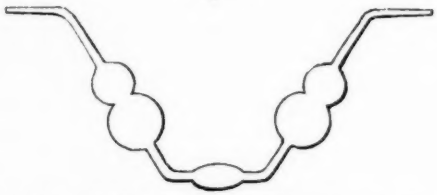



Fig. 2. A B black lead crucibles. C the upper opening. D the lower opening. E the cupel. The dotted semicircle represents the position of the furnace-door.

*Improved Form of Messrs. Will's and Varrentrapp's Apparatus.*

The only inconvenience I have found in the process proposed by Drs. Will and Varrentrapp for the estimation of nitrogen in organic bodies, is the liability of the liquid in the condenser being thrown back into the combustion-tube by sudden absorption taking place, or from too violent an evolution of the gases, part of it being ejected from the other extremity of the condenser. So well-aware were its authors of this inconvenience, that they recommend in the analyses of substances rich in nitrogen the introduction of sugar, or some other body abounding in carbon, into the combustion-tube. I have found that the necessity of this addition, which is of course open to many objections, may be entirely avoided by using a condenser nearly three times as large as that generally employed, and by surmounting each of the bulbs with another bulb of about half its capacity. The opening between the bulbs should be very wide, they being run into one another in the same manner as in the lower bulbs of Liebig's potash apparatus. With a condenser of this description, the large bulbs being $1\frac{3}{4}$ inch in diameter and about 4 inches apart, I have never experienced the least accident, nor am I compelled to pay that constant attention to the progress of the combustion which Drs. Will's and Varrentrapp's condenser usually requires.

Fig. 3.



Mr. Taylor also exhibited a small instrument for holding Daguerreotype plates during the process of washing off. It consisted of two pieces of brass or plaited wire fitted into a wooden handle. One of the wires is bent into the form of an acute triangle, its base being slightly turned up, so as to form a ledge for the silver plate to rest upon. The other wire is placed between the sides of the triangle curved, so as to form a spring, which rests upon the top of the plate, and keeps it in its place. By inserting the fore-finger in the loop of the spring, the plate may be shaken violently without becoming dislodged.

Fig. 4.



February 1, 1847.—James Lowe Wheeler, Esq., in the Chair.

The following communications were read:—

Note on the means of testing the comparative value of Astringent Substances for the purposes of Tanning. By Robert Warington, Esq.

Having been frequently called upon to examine the value of astringent substances imported into this country for the purposes of tanning, such as valonia, divi-divi, sumac, cutch, &c., I am induced to believe that the detail of the manipulation adopted may not be without interest to some of the members of the Society. As the manufacture of leather was the object of the purchaser of these materials, gelatin was selected as the basis for the estimation of their comparative value; and after several trials with various kinds of natural and manufactured gelatin, such as varieties of isinglass, glue, patent gelatin, &c., the finest long staple isinglass was found to be the most constant in its quality and least liable to undergo change.

With this therefore the test solution was prepared, of such a strength, that each division, by measure in the ordinary alkalimeter tube, should be equivalent to the one-tenth or one-fourth of a grain of pure tannin, and thus the number of divisions used would indicate the proportion of available tannin or substance precipitable by gelatin contained in any specimen. A given weight of the sample under trial was then infused in water, or if necessary the astringent matter extracted by boiling, and the clear liquid precipitated by the test solution until no further deposit occurred.

It was necessary in the course of this operation to test at intervals a portion of the solution under examination, to ascertain the progress of the trial; and this, from the nature of the precipitate, was attended at first with some little difficulty: paper filters were inadmissible from the quantity of the solution they would absorb, and thus introduce a source of extensive error; subsidence rendered the operation very tedious. The plan I have adopted is as follows:—a piece of glass tubing, about twelve inches in length and about half an inch internal diameter, is selected, and this has a small piece of wet sponge loosely introduced into its lower extremity, and when it is wished to abstract a part of the fluid under investigation for a separate testing, this is immersed a few seconds in the partially precipitated solution; the clear liquid then filters by ascent through the sponge into the tube, and is to be decanted from its other extremity into a test glass; if on adding a drop of the gelatin solution to this a fresh precipitate is caused, the whole is returned to the original bulk, and the process proceeded in, and so on until the operation is perfected; this method of operating is facilitated by conducting the examination in a deep glass. After a few trials the manipulation will be found extremely easy, and in this way considerable accuracy may be arrived at.

## CLXXXIX. *On the Action of a mixture of Red Prussiate of Potash and Caustic Alkali upon Colouring Matters.* By JOHN MERCER, *Esq.*

ABOUT ten years since I discovered and used extensively in calico-printing the oxidizing properties of a mixture of red prussiate of potash and caustic alkali. For many years I have been in the habit of communicating to my friends several applications of this interesting reaction, among whom I may mention Mr. Crum of Glasgow and Dr. Lyon Playfair. Since then Boudault * has directed attention to the oxidizing power of the same mixture, as far as relates to metallic oxides, but has not shown any important practical application of the knowledge thus acquired.

There are but few processes known in the arts for bleaching indigo, the principal of these being that in which chromic acid liberated from the bichromate of potash by means of an acid is used. In certain cases this process is attended with various disadvantages, and the cloth requires to be subjected to a clearing process to remove the oxide of chromium. The topical application of a mixture of red prussiate of potash and an alkali at once effects the same purpose, and in a most complete manner, leaving a brilliant white on the spot where the colour is discharged without rendering any injury to the fabric. The manner of applying this discharge may be arranged to suit the conditions of the calico-printer. As a class experiment for a lecture-table it is convenient to impregnate the indigo-blue calico with a solution of prussiate of potash, and then dip it into a weak solution of alkali.

This action is a beautiful illustration of those double affinities which we frequently find at play in combinations or decompositions. Thus, though neither chlorine nor charcoal can decompose alumina *per se*, the same gas passed over a mixture of alumina and charcoal combines with the metallic radical; the charcoal in this case having aided the combination by withdrawing the oxygen. It is the same kind of action in the case under consideration. Red prussiate of potash, $Fe_2\,Cy_6\,3K$, differs from the yellow prussiate, $Fe_2\,Cy_6\,4K$, by containing one atom less potassium. When potash is presented to the former, this deficient atom of potassium is supplied, but the affinity is not strong enough to liberate the oxygen. When however a second body having an attraction for oxygen, such as litharge or indigo, is presented to the potash and red prussiate, this second affinity acting in a different direction withdraws the oxygen and

* *Journal de Pharmacie.*

allows the potassium to unite with the compound radical ferrocyanogen; thus $Fe_2\ Cy_6\ 3K + KO + PbO = Fe_2\ Cy_6\ 4K + PbO_2$, the decomposition being of the same kind when an organic matter is substituted for the oxide capable of further oxidation. Soda and ammonia may be substituted for potash in the above decomposition, producing the oxidation or discharging the indigo. This is curious in the case of ammonia, for it cannot be explained by any other than by the ammonium theory, and shows the complete analogy between the oxide of ammonium and the oxide of the simple metallic radicals, potassium and sodium. It is interesting also to observe that the last member in the formula $Fe_2\ Cy_6\ 4R$, may be substituted by any alkaline base. Thus, that it may either be $Fe_2\ Cy_6\ 3K\ K$, or $Fe_2\ Cy_6\ 3K\ Na$, or $Fe_2\ Cy_6\ 3K\ NH_4$. This circumstance points to important theoretical considerations in the atomic constitution of the prussiates, which would be foreign to the present paper, the principal object of which is to furnish a means of discharging indigo, and thus supply a process much wanted in the art of calico-printing, and which I have followed for many years with success.

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Feb. 15, 1847.—Lieut. Col. Ph. Yorke, R.E., in the Chair.

Mr. Scanlan announced that he had found Iodide of Cyanogen in a specimen of the Iodine of commerce, to the extent of 100 grains in the pound weight.

The following paper was read:—

## CXC. *On the Composition of Caffein, and of some of its Compounds.* *By* Edward Chambers Nicholson, *Esq.*

CAFFEIN was first analysed by Professors Liebig and Pfaff* in 1832. The result of this investigation was confirmed by a subsequent analysis of Prof. Wöhler†.

In 1838 Professor Liebig induced M. Jobst‡ to analyse thein, who proved this body to be identical with caffein. His analyses gave the same results as his predecessors. The same remark applies to the experiments of Mulder§ on thein, and also to an analysis which M. Martius‖ made of guaranin, a substance, the identity of which with caffein and thein had previously been pointed out by Berthemot and Dechastelus¶. Lately Dr. Stenhouse**, when examining Paraguay tea, has also made some analyses of thein.

* Liebig's *Annalen*, i. 17. † Ibid. ‡ Ibid. xxv. 63.
§ *Bulletin des Sciences Phys. et Nat. de Neerlande.* 1838, p. 32.
‖ Liebig's *Annalen*, xxxvi. 93. ¶ Ibid. xxxvi. 90.
** Transactions of the Chemical Society, vol. i. pp. 215, 237.

The following table, in which I have recalculated these analyses according to the atomic weights, carbon 6 and hydrogen 1, allows a comparison to be made of the results obtained by these chemists.

*Mean of the Analyses.*

| | Caffein. | | Thein. | | | Guaranin. |
|---|---|---|---|---|---|---|
| | Liebig & Pfaff. | Wöhler. | Mulder. | Jobst. | Stenhouse. | Martius. |
| Carbon . | 49·30 | 49·25 | 49·18 | 49·47 | 48·95 | 49·23 |
| Hydrogen | 5·22 | 5·43 | 5·49 | 5·20 | 5·15 | 5·08 |
| Nitrogen . | 28·86 | | 28·53 | 28·90 | | 28·83 |

The most simple expression which can be deduced from these numbers is

$$C_8 H_5 N_2 O_2.$$

Stenhouse's analysis however of the platinum compound proves that this formula must be doubled, and that the atom of caffein or thein is

$$C_{16} H_{10} N_4 O_4.$$

The theoretical numbers of this formula are the following:—

| | | | |
|---|---|---|---|
| 16 eqs. | Carbon . . . | 96 | 49·48 |
| 10 ... | Hydrogn . . | 10 | 5·15 |
| 4 ... | Nitrogen . . | 56 | 28·86 |
| 4 ... | Oxygen . . . | 32 | 16·51 |
| | | 194 | 100·00 |

From these numerous experiments the composition of caffein might have been considered as perfectly established. In a recent investigation of coffee, however, M. Payen* states that he has obtained results which differ very sensibly from those obtained by his predecessors, and which he has translated into the formula

$$C_{16} H_{10} N_4 O_3,$$

which contains 1 equiv. of oxygen less than the formula up to the present time admitted.

The theoretical numbers of Payen's formula are—

| | | | |
|---|---|---|---|
| 16 eqs. | Carbon . . . | 96 | 51·43 |
| 10 ... | Hydrogen . . | 10 | 5·35 |
| 4 ... | Nitrogen . . | 56 | 30·34 |
| 3 ... | Oxygen . . . | 24 | 12·88 |
| | | 186 | 100·00 |

We observe here a difference of 2 per cent. of carbon, which

* *Comptes Rendus de l'Académie*, tome xxiii. 8.

M. Payen has obtained over the results of the above-mentioned chemists.

In order to elucidate this discrepancy, Dr. Hofmann induced me to make some experiments under his direction, partly with a quantity of beautiful caffein which he gave me* and partly with a specimen which I have prepared myself.

### *Caffein.*

To ensure perfect purity of the substance it was crystallized three times from dilute alcohol, washed and dried. Thus purified, it formed very beautiful long white prisms, perfectly transparent when dried in the air, but which became opake if exposed to a higher temperature. The crystals dried in the water-bath lost no weight when kept in an air-bath for four hours at a temperature of 130° C.

The specimen which I had prepared myself was obtained from Costa Rico coffee, by boiling the bruised fruit in water, precipitating the decoctions by basic acetate of lead and treating the filtrate with hydrosulphuric acid; after the whole of the lead had been removed, I evaporated the liquid to dryness in a water-bath, in order to get rid of acetic acid, and dissolved the residue in a small quantity of boiling water: upon cooling, the caffein crystallized out of a dark colour, and very impure. To purify it, it was washed and recrystallized three times from water, and finally from alcohol. It was then perfectly white, and had exactly the same appearance as the specimen which I obtained from Dr. Hofmann.

### *Analysis.*

I. 0·3827 grm. of substance, dried at 100° C. and burnt with chromate of lead, gave 0·6948 grm. of carbonic acid, and 0·1800 grm. of water.

II. 0·417 grm. of substance, burnt with chromate of lead and chlorate of potash, gave 0·7552 grm. of carbonic acid, and 0·1965 grm. of water.

III. 0·3934 grm. of substance of my own preparation gave 0·7123 grm. of carbonic acid and 0·1878 grm. of water, which calculated in 100 parts gives—

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . . | 49·51 | 49·39 | 49·37 |
| Hydrogen . . | 5·22 | 5·23 | 5·30 |

* I owe this specimen, of great beauty, to the well-known kindness of Mr. E. Merck of Darmstadt.—A. W. H.

which agrees with Professor Liebig's formula, as is seen by the following:—

| | | | Theory. | Mean of experiments. |
|---|---|---|---|---|
| 16 eqs. | Carbon . . . | 96 | 49·48 | 49·42 |
| 10 ... | Hydrogen . . | 10 | 5·15 | 5·28 |
| 4 ... | Nitrogen . . | 56 | 28·86 | |
| 4 ... | Oxygen . . . | 32 | 16·51 | |
| | | 194 | 100·00 | |

*Caffein and Bichloride of Platinum.*

On precipitating a solution of caffein in hydrochloric acid with bichloride of platinum, as Dr. Stenhouse has shown, a precipitate of an orange-yellow colour is obtained. If the two solutions are mixed hot, the fluid on cooling deposits the compound in beautiful granular crystalline tufts, which, when thrown on a filter and washed with alcohol, are perfectly pure. This double salt is only sparingly soluble in alcohol, æther, and water. It does not alter when exposed to light, nor does it lose in weight when kept at 100° C. for a considerable time.

The analyses of salts, all prepared at different periods and dried at 100° C., gave the following results:—

I. 0·5382 grm. of substance, burnt with chromate of lead, gave 0·4765 grm. of carbonic acid, and 0·1387 grm. of water.

II. 0·4881 grm. of substance gave 0·1196 grm. of platinum.

III. 0·4779 grm. of substance gave 0·1172 grm. of platinum.

IV. 0·6022 grm. of substance gave 0·1482 grm. of platinum.

V. 0·5781 grm. of substance gave 0·1425 grm. of platinum.

VI. 0·5246 grm. of substance gave 0·1293 grm. of platinum.

VII. 0·3847 grm. of substance made of caffein of my own preparation, gave 0·0945 grm. of platinum.

Which give the following per-centages:—

| | I. | II. | III. | IV. | V. | VI. | VII. |
|---|---|---|---|---|---|---|---|
| Carbon | 23·80 | | | | | | |
| Hydrogen | 2·86 | | | | | | |
| Platinum ... | | 24·51 | 24·52 | 24·60 | 24·64 | 24·64 | 24·56 |

leading exactly to the formula given by Dr. Stenhouse, viz.

$$C_{16}\,H_{10}\,N_4\,O_4\,HCl,\,Pt\,Cl_2,$$

as is seen when placed in comparison with the calculated numbers.

| | | | Theory. | Mean of my experiments. | Dr. Stenhouse's mean. |
|---|---|---|---|---|---|
| 16 eqs. | Carbon . . | 96·0 | 23·97 | 23·80 | 24·22 |
| 11 ... | Hydrogen . | 11·0 | 2·74 | 2·86 | 2·89 |
| 4 ... | Nitrogen . | 56·0 | 13·98 | | |
| 4 ... | Oxygen . . | 32·0 | 8·02 | | |
| 3 ... | Chlorine . . | 106·5 | 26·59 | | |
| 1 ... | Platinum . | 98·9 | 24·70 | 24·58 | 24·49 |
| 1 ... | Caffein and bichloride of platinum | 400·4 | 100·00 | | |

The analysis of caffein, as well as that of the platinum compounds, agree so perfectly with the numbers of Professor Liebig's formula, that there can be no doubt about its accuracy.

Assuming 1 equiv. of oxygen less in the equivalent of caffein, as is proposed by M. Payen, the platinum compound should contain not less than 24·46 per cent. of carbon and 25·12 of platinum. Now three determinations by Dr. Stenhouse, and six which I have made, never gave more than 24·64 per cent., that is, 0·6 per cent. less of platinum.

Not satisfied, however, with these proofs, I have tried to find some other compounds by which the atomic weight of caffein could be determined with equal accuracy.

In what follows a description of several new double salts of caffein will be given, the analyses of which correspond equally well with the original formula of this substance.

### *Caffein and Nitrate of Silver.*

This compound is obtained when a solution of nitrate of silver is added in excess to an aqueous or alcoholic solution of caffein. If the solutions are concentrated it falls down in white hemispherical nodules, which adhere firmly to the side of the vessel.

When washed with water and crystallized from alcohol it is absolutely pure. This compound is indistinctly crystalline, of a perfectly white colour, and if dry undergoes no change when exposed to light, but if moist acquires a purplish hue. It is very soluble in hot water and alcohol, sparingly soluble in cold, and may be boiled in either solvent without undergoing decomposition. It loses no weight in the water-bath, but at a higher temperature it is decomposed, caffein sublimes, and metallic silver is left.

*Analysis.*—When burnt with chromate of lead—

I. 0·4514 grm. of substance gave 0·4345 grm. of carbonic acid, and 0·1162 grm. of water.

II. 0·2500 grm. of substance gave ·0744 grm. of silver.

III. 0·2716 grm. of substance gave ·0810 grm. of silver, which give the following per-centages:—

| | I. | II. | II. |
|---|---|---|---|
| Carbon . . . | 26·45 | | |
| Hydrogen . . | 2·86 | | |
| Silver . . . | ... | 29·76 | 29·82, |

and the formula—$C_{16}H_{10}N_4O_4+AgO,NO_5$, as may be seen by the following calculation:—

| | | | Theory. | Found. |
|---|---|---|---|---|
| 16 eqs. | Carbon . . . | 96 | 26·37 | 26·45 |
| 10 ... | Hydrogen . . | 10 | 2·74 | 2·86 |
| 5 ... | Nitrogen . . | 70 | 19·23 | |
| 10 ... | Oxygen . . | 80 | 22·00 | |
| 1 ... | Silver . . . | 108 | 29·66 | 29·79 |
| | | 364 | 100·00 | |

The only analogues to this singular compound which I know are those of urea and nitrate of silver, analysed by Werther*: the formulæ of which are—$C_2H_4N_2O_2+AgO,NO_5$, and $C_2H_4N_2O_2+2(AgO,NO_5)$.

These compounds, however, in consequence of the peculiar nature of urea, are not very stable, being decomposed when boiled with water into nitrate of ammonia and cyanate of silver. There likewise exists a compound of nitrate of silver and glycocoll, lately described by Horsford†, having the formula

$$C_4H_4NO_3+AgO,NO_5;$$

and, according to H. Rose, a compound of nitrate of silver with ammonia, 3 equivs. of this gas being absorbed by 1 equiv. of the former salt.

### *Chloride of Mercury and Caffein.*

This beautiful compound is obtained when an aqueous or alcoholic solution of caffein is added to a solution of chloride of mercury; the latter being kept in excess, the fluid remains perfectly clear, but after the lapse of a few seconds solidifies into a mass of very small crystals, which when recrystallized from water or alcohol and washed on a filter, are quite pure.

When pure and crystallized from water it is very similar in appearance to caffein, the crystals not being however quite so large. It is very soluble in alcohol and water, hydrochloric, nitric, and oxalic acids, and seems to form with the latter a crystalline compound. It is nearly insoluble in æther. In reference to its constitution, it is distinguished from the dou-

* Liebig's *Annalen*, lvi. 262. † Ibid. lx. 36.

ble salt of platinum, for in this instance the caffein is in direct combination with the chloride of mercury, and is exactly analogous to the corresponding compounds of leucoline and aniline investigated by Dr. Hofmann*. The mercurial compounds of this kind are generally easily decomposed, but the compound of chloride of mercury and caffein is so stable, that it may be boiled in water for a considerable time without undergoing the slightest change in its properties. It may be dried at 100° C. and loses no weight at that temperature.

I endeavoured to combine the determination of the carbon, hydrogen and mercury of this substance in *one* combustion, and have perfectly succeeded. The operation was conducted as follows:—The substance was mixed with chromate of lead and introduced into a combustion-tube of at least 26 inches in length. About 6 inches of copper turnings are placed above the mixture, leaving a space of 8 inches from the copper to the anterior end of the tube. A receptacle for the mercury is formed out of the tube itself by contracting it about an inch from the copper turnings, and again so as to leave an elongated bulb of an inch in length. At the close of the operation the tube is cut with a file at the posterior contraction. In order to separate the water from the mercury, the chloride of calcium tube (which has not been detached) is connected with an aspirator and air admitted through chloride of calcium, the bulb being kept at a temperature of 100° C.

I obtained in my analysis the following numbers:—0·7833 grm. of substance gave 0·5832 grm. of carbonic acid, 0·1639 grm. of water, and 0·3365 grm. of mercury, corresponding to the following per-centage, which I place in comparison with the theoretical numbers:—

| | | | Theory. | Expt. |
|---|---|---|---|---|
| 16 eqs. | Carbon | 96 | 20·68 | 20·30 |
| 10 ... | Hydrogen | 10 | 2·15 | 2·32 |
| 4 ... | Nitrogen | 56 | 12·11 | |
| 4 ... | Oxygen | 32 | 6·89 | |
| 2 ... | Chlorine | 70 | 15·08 | |
| 2 ... | Mercury | 200 | 43·09 | 42·91 |
| | | 464 | 100·00 | |

### *Caffein and Terchloride of Gold.*

This compound is formed when a solution of terchloride of gold is added in excess to caffein dissolved in dilute hydrochloric acid. If concentrated solutions are employed, the whole immediately solidifies into a mass of a most splendid lemon-yellow colour; this is to be washed with cold water

* Liebig's *Annalen*, xlvii. 37.

and crystallized from alcohol, and finally dried in the water-bath.

The crystals from an alcoholic solution are in the form of long needles, of an orange-yellow colour and a very bitter metallic taste; they are soluble in alcohol and water. When boiled in water for a short time, the salt is decomposed, a yellow flocculent matter precipitating, which is insoluble in alcohol, ether and water, but soluble in hydrochloric acid. If an aqueous solution is kept on the sand-bath for some hours at a temperature of about 68° C. it is also decomposed, and metallic gold separates in shining scales.

It is not altered when exposed to light, and when dry may be heated to 100° C. without undergoing decomposition.

*Analysis.*—When burnt with chromate of lead—

I. 0·8530 grm. of substance gave 0·5525 grm. of carbonic acid and 0·1622 grm. of water.

II. 0·3224 grm. of substance gave 0·1197 grm. of metallic gold.

III. 0·3019 grm. of substance gave 0·1115 grm. of metallic gold, which give the following per-centages:—

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . | 17·72 | | |
| Hydrogen . | 2·11 | | |
| Gold . . . | | 37·12 | 36·93 |

corresponding to the formula $C_{16}H_{10}N_4O_4HClAuCl_3$, as may be seen by the following table, where the calculated and quantities found are placed in comparison:—

| | | | Theory. | Found. |
|---|---|---|---|---|
| 16 eqs. | Carbon . | 96·00 | 17·98 | 17·72 |
| 11 ... | Hydrogen | 11·00 | 2·06 | 2·11 |
| 4 ... | Nitrogen . | 56·00 | 10·50 | |
| 4 ... | Oxygen . | 32·00 | 6·01 | |
| 4 ... | Chlorine . | 142·00 | 26·60 | |
| 1 ... | Gold . . | 196·66 | 36·85 | 37·02 |
| | | 533·66 | 100·00 | |

The caffein compounds which I have analysed are therefore—

| | |
|---|---|
| Caffein . . . . . | $C_{16}H_{10}N_4O_4$. |
| Platinum compound | $C_{16}H_{10}N_4O_4$, $HClPtCl_2$. |
| Silver compound . | $C_{16}H_{10}N_4O_4$, $AgO$, $NO_5$. |
| Mercury compound | $C_{16}H_{10}N_4O_4$, $2(HgCl)$. |
| Gold compound . . | $C_{16}H_{10}N_4O_4HCl$, $AuCl_3$. |

There exist several other double compounds of caffein, which I have however not subjected to analysis.

On mixing a hot alcoholic solution of caffein with an alcoholic solution of cyanide of mercury, beautiful needles of a double salt are deposited upon cooling, which correspond most likely to the mercury salt I have just described. A solution of caffein in hydrochloric acid gives a beautiful brown precipitate with chloride of palladium; and the filtered solution deposits another compound in the form of yellow scales, very similar in appearance to iodide of lead.

Caffein gives no precipitate with solutions of sulphate of copper, chloride of tin, acetate of lead, and nitrate of suboxide of mercury. When boiled with sesquichloride of iron, a reddish-brown precipitate subsides upon cooling, which is perfectly soluble in water, and is most likely a double compound of caffein and sesquichloride of iron.

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March 1, 1847.—The President in the Chair.

The following letter was read from Mr. Coathupe of Bristol:—

"I herewith send you two specimens of gun-cotton, with a view to illustrate the greatly increased explosive effects that are to be derived from a subsequent immersion of the gun-cotton, when properly prepared in the ordinary way, in a saturated solution of chlorate of potash.

"Having experimented with solutions of nitrate of ammonia, nitrate of potash, nitrate of soda, bichromate of potash, &c. &c., for the purpose of increasing the explosive properties of this interesting substance, I can affirm that none of the results will bear the slightest comparison with those obtained from the solution of chlorate of potash, either in rapidity of ignition or in intensity of flame. The process adopted for preparing the inclosed specimens was as follows: viz. into a mixture of equal measures of strong *nitrous* acid and of oil of vitriol, spec. grav. 1·845, the cotton was immersed and stirred with a glass rod during about three minutes: it was then well-washed in many waters and dried; a portion of it was then soaked for a few minutes in a saturated solution of chlorate of potash, well-squeezed and dried."

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March 15, 1847.—The President in the Chair.

Presents were announced—

"On the Motion of Gases, by Thomas Graham," from the author.

"Note on the Examination of the Waters of Towns for its Hardness, by Thomas Clark, M.D.," from the author, accompanied by several numbers for distribution to the Members.

The following papers were read:—

## CXCI. *On the Preparation of Hippuric Acid.* By William Gregory, *M.D.*

SINCE the discovery of hippuric acid by Liebig, that body has at all times attracted much attention. Its composition and the products of its decomposition, among which were benzoic acid and benzamide, rendered it interesting, and various ingenious views were entertained of its constitution. Its detection in human urine by Liebig gave it additional importance.

The beautiful discovery of Dessaignes, that hippuric acid, when heated with strong acids, is resolved into benzoic acid and glycocoll, has greatly increased the interest already attached to hippuric acid, which now affords the best means of obtaining glycocoll, and has enabled Horsford, in his elaborate researches on that substance, to fix its formula in a very satisfactory manner.

| | |
|---|---|
| If to hydrated hippuric acid . | $C_{18}\,N\,H_9\,O_6$, |
| we add 1 equiv. water . . . | $H\;O$, |
| and from the sum . . . . . | $C_{18}\,N\,H_{10}\,O_7$, |
| subtract 1 equiv. glycocoll . . | $C_4\;N\,H_4\;O_3$, |
| there remain . . . . . | $C_{14}\;\;H_6\;O_4$, |

which is hydrated benzoic acid.

There cannot, I think, be any longer a doubt that $C_4\,N\,H_4\,O_3$ is the true formula of glycocoll, and Horsford has, in establishing this point, at the same time confirmed and explained in the most satisfactory manner the observation of Dessaignes.

The researches of Horsford, however, have also demonstrated that glycocoll is in itself one of the most interesting compounds known to chemists, and it is evident that the further study of this most singular body will lead to very valuable results.

I have already stated that glycocoll is best obtained from hippuric acid, but as soon as I began to prepare for this purpose a considerable quantity of hippuric acid, I found, as all who have done so must have found, that the operation as prescribed in books is not only tedious and troublesome, but uncertain.

The usual process consists in evaporating the urine of the horse or cow at a moderate temperature to about one-eighth of its bulk, and adding hydrochloric acid, when on standing a few hours, crystals of impure hippuric acid are deposited. But it is well-known that if the temperature should rise too high, although still to a point short of boiling, the hippuric acid will partially or totally disappear, and benzoic acid will be found in its place. Now when we bear in mind that the

urine contains but little hippuric acid, it is evident that to obtain this acid in quantity we must operate with a very large bulk of urine, and those who have done so well know how tedious the evaporation is, since if we attempt to hasten it by raising the temperature, we run the risk of losing the whole; and this indeed frequently happens.

The impure, highly-coloured acid first obtained has been purified by different chemists in a great variety of ways. Some have used chloride of lime; but this method is not easily managed, and often converts the whole into benzoic acid.

The last and by far the best method of purification is that of Schwarz, who boils the impure acid with an excess of milk of lime, and strains the alkaline liquid from the undissolved lime. It passes rapidly and clear through calico, and the lime retains the colouring matter, so that the addition of acid to the filtered liquid causes the deposition of crystals of hippuric acid nearly white. Schwarz recommends the addition of chloride of calcium to the filtered or unfiltered liquid, and the precipitation of the lime as carbonate by carbonate of potash or soda, when the precipitated carbonate of lime carries with it the last traces of colouring matter. I have not found this necessary, as a repetition of the process with the milk of lime never fails to yield colourless crystals.

As it was clear that the hippuric acid was not in the slightest degree decomposed by boiling with excess of lime, although so easily metamorphosed by acids, I thought that by applying the same principle to the urine directly, I might be enabled *to boil it down*, and thus shorten the process, and at the same time prevent the decomposition of the hippuric acid, since it would appear that hippurate of lime is not affected by boiling, nor by excess of lime.

Accordingly, I took some urine of the horse, mixed it with excess of milk of lime and boiled for a few minutes. I then strained the solution, which was very materially decolorized, and boiled the clear liquid as rapidly as possible down to the requisite bulk. On adding hydrochloric acid I obtained a copious deposit of crystals, which when pressed had a slight red colour. I then treated them by Schwarz's method and obtained an abundant crop of almost colourless crystals, which consisted entirely of the needles of hippuric acid, without a visible trace of benzoic acid, the crystallization of which is easily recognized. A second treatment with milk of lime, which was hardly needed, and probably would have been quite unnecessary had a greater excess of lime been used in the previous one, yielded snow-white crystals of the utmost beauty and purity.

The improvement which I have thus introduced in the preparation of hippuric acid may seem trifling, and is indeed only the application of Schwarz's method to the urine, instead of to the crude acid; but any one who tries to prepare some ounces, not to say pounds, of hippuric acid, will soon find that the difference is practically important. By my method it is possible to extract in one day the hippuric acid from as much urine as would require a week to operate upon on the usual plan, so that the quantity of hippuric acid which we can thus obtain is only limited, as it were, by the quantity of urine to be procured. The tedious evaporation at low temperatures is got rid of, and we are sure of obtaining the whole hippuric acid originally present; whereas, on the former plan, however carefully the evaporation is conducted, and it requires constant superintendence, it almost always happens that some of the hippuric acid is decomposed; while a very slight accidental rise of temperature may destroy the whole of it, as I have often seen.

On the whole, I am satisfied that all who wish to study hippuric acid and glycocoll will find on trial that what was formerly a disagreeable and troublesome operation is now a very easy and short one; and that they may now easily obtain these remarkable compounds in any desired quantity.

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## CXCII. *On the Decomposition of Water by Platinum and the Black Oxide of Iron at a white heat, with some observations on the theory of Mr. Grove's Experiments.* By George Wilson, *M.D.*

THE remarkable discovery recently made public by Mr. Grove, that water in certain circumstances, when raised to a white heat, is resolved into its constituent gases, has naturally excited much attention. It furnished the unexpected confirmation of the truth of an opinion expressed by James Watt so far back as 1783, that if steam could be made red hot [white hot] so that all its latent heat should be converted into sensible heat, either the steam would be converted into permanent air, or some other change would take place in its constitution *.

In the greater number of Mr. Grove's experiments, water was raised in temperature through the medium of platinum; and it became a question accordingly, as Sir John Herschel and my friend Dr. Lyon Playfair suggested, how far the decomposition of water observed was owing to the mere heat of

* Phil. Trans. 1783, p. 416.

the metal, how far to the peculiar surface-influence, or so-called catalytic force, which has been so long recognized as possessed by platinum and the other noble metals. Dr. Playfair also referred to the fact, "that many bodies at high temperatures exhibited a great affinity for oxygen, which they did not possess at lower temperatures; as, for instance, silver, gold, and even platinum itself, which metals absorb oxygen when intensely heated, and give it out again on cooling. If the experiments had been tried in tubes of quartz or silica, they would not have been open to the objection which the use of so peculiar a metal as platinum appeared to involve*."

There was indeed one form of Mr. Grove's experiment not liable to the exception urged against those where platinum was used. He found it quite possible to decompose steam by sending Leyden-jar discharges through it, and refers the decomposition solely to the heat evolved by the electric spark. The same view has been suggested as not improbable by Faraday, in relation to the decomposition of water in the liquid form by electric discharges †. With great diffidence, however, I would remark, that the spark decomposition of water cannot be regarded as an *experimentum crucis*. Although the electric spark cannot decompose steam electrolytically, we may not at once infer that it cannot decompose it in another way. I have no wish to assert that it can, but it is possible that it may, and a crucial experiment should be unexceptionable. Again: the spark discharge of a Leyden jar exerts a great disruptive force, and acts topically with much violence. There is reason moreover to believe that mechanical agitation or disturbance of a chemical compound can in many cases cause the separation of its elements. It may seem an extravagant idea to suppose that oxygen may be torn or detached from hydrogen by the action of a disruptive force on the molecules of water, as if chemical affinity were but a kind of mechanical cohesion, which may be overcome by division. On the other hand, however, it must not be forgotten, that we are now acquainted with a large number of fulminating compounds, which can be decomposed by friction, by a touch, or a stroke. These compounds are all fragile, and water is a very stable combination; but fragility and stability are but terms of degree, in relation to stability of union: and if it shall appear that a feeble mechanical force can overcome a small intensity of affinity, it will be acknowledged as quite possible that a powerful mechanical agency may overcome a great one. We have no means perhaps of

* Athenæum for September 19th, 1846, p. 966.

† Researches in Electricity, 3rd series, paragraph 337.

making an unexceptionable experiment as to the decomposing power of mechanical force; for we cannot bring it into play without calling into action other agencies. If we touch, or rub, or strike a fulminate, for example, we cause the evolution of heat, and add its decomposing power to that of the mechanical impulse. It would be a mere *petitio principii*, however, to assume that the heat produced alone effects the decomposition observed. It seems to me, therefore, that the decomposition of steam by the electric spark furnishes a more complex problem for solution than the action of white-hot platinum on the same compound does; and that the experiments made with the metal are more likely to throw light on those tried with the spark, than to be explained by them.

Whilst thinking over these difficulties, and the objections to Mr. Grove's conclusions suggested by Herschel and Playfair, I had occasion to perform the familiar class-experiment of burning iron wire in oxygen. I observed with an interest I had not felt previously, although I had carelessly noticed the phænomenon before, that bubbles of apparently permanent gas rose from the globules of white-hot oxide of iron as they fell into the water. It seemed to me possible that this gas might be a mixture of oxygen and hydrogen separated by the influence of the metallic oxide, acting as platinum did in Mr. Grove's experiments. It was certain, moreover, that if this should prove to be the case, it would supply a powerful argument in favour of that gentleman's conclusion, which seems, in spite of all the objections noticed, in the highest degree probable, namely, that heat, apart altogether from the medium through which it is applied, can resolve water into its elements.

As the following experiments were made solely in the hope of substantiating Mr. Grove's view, which unfortunately, however, they leave exactly as they found it, I trust that gentleman will not consider their publication an interference with his researches. I was led to try them incidentally, and abandoned them as soon as I found I could render Mr. Grove no assistance by means of them.

It would be difficult to conceive a more rapid and effectual way of raising a body to a white heat than that afforded by the combustion of iron in oxygen. I took for granted also (as it afterwards appeared, too hastily) that the metal could not but be saturated with oxygen and converted into a definite oxide, which would be chemically indifferent to each of the elements of water, and if it decomposed it at all, would reject both its constituents. The convenient way, moreover, in which the globules of oxide detach themselves and fall

into the water, and the rapidity with which the whole process goes on, make it a very easy matter to collect in considerable quantity whatever gases are evolved. A stoppered bottomless jar of the ordinary construction for the iron-wire experiment, and of 291 cubic inches' capacity, was made use of in the following trials. Eighteen experiments were made with it, and from 100 to 110 grains of fused globules were obtained from each combustion. A test-tube, with a funnel fixed into it by a perforated cork, and filled with water, was arranged so as to receive the gas. In some experiments it was placed within the oxygen jar, so that the coil of wire when introduced hung close to it, a piece of tin plate being arranged so as to guide the globules within the edge of the inverted funnel. In the greater number of trials however the tube and funnel were placed outside of the vessel containing the oxygen, and an inclined plane of tin plate was so placed as to carry the globules past the edge of the jar, and within the mouth of the funnel. No difference of result was observed in experiments made in both ways, but the latter arrangement was preferred as more convenient, and as enabling more oxygen to be employed at each trial.

In all the experiments, permanent gas was evolved when the fused globules fell into the water. This statement is to be considered as applying to each combustion considered as a whole; for individual globules were frequently observed to give off no gas at all, or to evolve so very little, that it might be air separating from the water, in which it had previously existed in solution. The quantity of gas obtained at each combustion varied greatly. Sometimes as much as a cubic inch was procured, more frequently only half that quantity, and occasionally less. The globules from thick coils of wire gave off a larger volume of gas than those from thin ones.

Portions of the gas were transferred to a Grove's eudiometer over water, and exposed to a white-hot platinum wire. They did not kindle or detonate, nor were they sensibly diminished in volume. Other portions were subjected to electric sparks and discharges in a syphon eudiometer over water, with the same negative results; but when air or oxygen was mingled with the gas, it exploded sharply with heated platinum or the electric spark. When a match was applied to the open end of a tube containing the unmingled gas, it burned rapidly with a pale blue flame, but did not explode. The gas given off during the action of the fused globules on water was not then a mixture of oxygen and hydrogen.

Its freedom from all but a trace of oxygen was ascertained in other ways. To one portion of the gas standing over water

nitric oxide was added, but no ruddy fume or yellow coloration showed itself. When phosphorus was introduced into the gas, in one instance it did not smoke, but in the greater number of cases it fumed for a brief period, and occasioned an amount of contraction barely perceptible. The gas appeared to be nearly pure hydrogen. To ascertain if it certainly were so, a portion of it was carefully dried, by chloride of calcium, and transferred to a eudiometer over warm mercury. Dry oxygen was then added, and the mixture exploded. When the whole had cooled, the walls of the eudiometer appeared dimmed by a very thin layer of moisture, but the quantity of gas operated on was too small to admit of visible drops being produced. Another portion of the gas was mixed with half its volume of oxygen and fired by the electric spark. The contraction which followed explosion varied in different experiments, but was frequently such as to leave not more than one-twentieth part of the mixed gases unconsumed. Phosphorus smoked in this residue for a short time, showing that excess of oxygen had been made use of, and left a minute volume of gas which was not diminished by caustic potash, and must have been nitrogen.

It seemed possible that the trace of carbon present even in malleable iron might affect the quality of the gas resulting from the action of the globules of oxide on water, and that carburetted hydrogen, carbonic oxide or carbonic acid might be produced. It seemed desirable to know whether the latter were present or not, as the oxygen might have gone to form them. It was impossible to be certain that carbonic acid was absent, for the gas from the globules being necessarily collected over water, the temperature of which was low, carbonic acid would be retained in solution by that liquid. All that I can say on this point is, that lime-water was not rendered muddy or in the slightest degree opalescent by the gas. It was several times detonated with oxygen over lime-water, but the latter remained quite transparent, so that neither carbonic oxide nor carburetted hydrogen can have been present. In short, the gas evolved from water by the white-hot globules of oxide of iron, was hydrogen mingled with a small quantity of air, previously no doubt in solution in water.

As only the hydrogen, then, of the water decomposed was obtained, it became necessary to account for the absence of the oxygen. I was tempted for a moment to think it possible that the black oxide of iron might have changed into the red oxide of the same metal, by combining with the oxygen not obtained in the elastic form: *ex. gr.* thus $2\,Fe_3O_4 + O = 3Fe_2O_3$.

But the proto-peroxide of iron is known to be a very stable compound, little if at all prone to become the peroxide; and it seemed more likely that unoxidized iron might be present in the fused globules, which occasioned the evolution of hydrogen when it came in contact with water. To ascertain this point, portions of the globules were dissolved in dilute muriatic and sulphuric acids, and were found in most cases to evolve hydrogen. Some specimens of the globules gave off not a trace of gas when they dissolved, and must have consisted of the definite oxide; a point of interest in connection with the fact already mentioned, that globules were frequently observed to drop into water without any bubbles of gas rising from them.

The volume of hydrogen however given off in some of the trials, when the product of combustion was placed in acid, was very considerable. A graduated gas jar was filled with dilute sulphuric acid, and inverted over a small capsule containing 100 grains of the crushed globules, which was placed in a basin also containing dilute acid. By this arrangement the gas was collected and measured at the same time, without risk of mixing with air, or necessity for watching the process, which is a slow one. 100 grains treated in this way gave off 16 cubic inches of hydrogen, corresponding to 9 grains of iron. The experiment was accidentally stopped at this point whilst the gas was still rising in undiminished quantity.

Metallic iron, then, was certainly present in many of the globules, and of this I had direct ocular demonstration. On crushing some of them in a mortar, they were found to separate into a shell of pulverizable oxide, and a core of iron which formed a nearly spherical pellet. In one case 50 grains of the globules were crushed, the pellets separated, and the residue placed in diluted sulphuric acid. It did not evolve a trace of hydrogen in the course of twenty-four hours. The pellets were then added to the same acid, and gave off 12 cubic inches of gas = 13·6 per cent. of iron in the globules*. The shell of oxide is frequently imperfect or perforated, so that water or any other liquid penetrates to the iron core, and is subject to its influence. When this becomes known, it need not surprise us that most of the globules should rapidly decompose water. After observing this fact, I tried the effect of thin and thick coils of wire, and found that the latter invariably gave off the greater volume of gas. When the coil is so thin that the metal all oxidizes, no gas is evolved at all. A thick coil indeed furnishes a striking mode of illustrating

* In none of the experiments was the thermometer or barometer specially observed, as minute accuracy was not aimed at.

to a class the principle of Lavoisier's mode of decomposing water, and forms a beautiful addition to the iron-wire experiment.

From these observations then, it would seem that white-hot oxide of iron cannot decompose water in the way white-hot platinum does. But before any conclusion can be drawn from this fact inimical to Mr. Grove's views, or favourable to the opinion that a specific property of the platinum has more to do with the decomposition of water than its mere temperature has, we should require to know how far the two white-hot bodies are to be considered as at the same temperature. In Mr. Grove's experiments, platinum is raised to as high a heat as it can bear without fusing. It must then be elevated to a temperature much above that necessary to make iron white hot, or to fuse its oxide, for our forges can melt iron and its oxides, but do not fuse platinum. It may also be remarked, that bright as the light emitted by burning iron is, it falls short in intensity of that given off by platinum on the verge of fusion. It seems accordingly probable, that during the combustion of iron in oxygen the temperature never rises high enough to confer upon the resulting oxide the power of decomposing water. The question admits of direct decision, by ascertaining whether oxide of iron, heated by the oxy-hydrogen blowpipe to as high a temperature as fusing platinum, acquires the power of decomposing water without appropriating to itself either of its elements. But it would have been an interference with Mr. Grove's own researches to have made experiments of this kind, and I have accordingly left the question undecided.

Meanwhile the experiments I have recorded are of some little interest, as at least showing that not only a white heat, but a high white heat, is essential to the successful performance of Mr. Grove's experiments. Unfortunately, we have not at present any method of measuring high temperatures which admits of ready application or secures great accuracy. "White heat" is in fact a vague expression for a range of temperature, of the extremes in either direction or extent of which we have no very precise knowledge. The power of the eye to measure the relative intensities of the light evolved by white-hot bodies is very limited, and varies greatly in different individuals. But the experiments I have recorded seem to supply the means of so far at least defining the white heat requisite for the separation of the elements of water, inasmuch as they show that it must at least exceed the temperature necessary for the fusion of malleable iron or its black oxide. If, moreover, the decomposing powers of the electric

spark be solely referable to its temperature, we seem entitled to conclude, from the experiments I have detailed, that the heat of the smallest spark that can decompose water is at least equivalent to that of fusing platinum. They appear also to warrant another conclusion. It was suggested by Dr. Leeson and by Mr. Hunt, that the bursting of steam-boilers might occasionally be owing to the metal they consist of becoming white-hot and decomposing water like platinum, with the rejection of both its elements*. This ingenious suggestion seemed to myself, before making experiments with iron, likely to prove just; but as fusing white-hot iron appears unable to decompose water, otherwise than by combining with its oxygen, it is impossible that the walls of a boiler can ever be raised to a temperature sufficiently high to enable them to separate the elements of water in the way platinum does.

I may now be permitted to make some comments on the rationale of the results obtained by Mr. Grove. That gentleman, if I understand him aright, considers the decomposition of water by white-hot platinum not only, as assuredly it is, a remarkable and unexpected result, but as evidencing on the part of heat a power to produce opposite or dissimilar chemical effects in the same circumstances. He is reported in the Athenæum (Sept. 19th, 1846, p. 966) to have "announced his discovery that all the processes by which water may be formed are capable of decomposing water" (p. 966). If by this statement be simply meant, that heat combines oxygen and hydrogen into water, and decomposes water into these gases, it will be admitted to be a just conclusion; but it may be questioned, I think, whether Mr. Grove's experiments add anything to our knowledge of the power of heat to effect chemical changes, except in so far as they supply an additional very remarkable example of its twofold analytical and synthetical agency, which has been so long recognised. Hydrogen, which as a gas is probably the vapour of a very volatile metal, may be compared with mercury, also a volatile substance. If mercury and oxygen be heated together to the temperature of 662° F., they combine and form the red oxide of the metal. If this resulting oxide be raised to a low red heat, it is decomposed into mercury and oxygen. In like manner, if hydrogen and oxygen be raised together to the temperature of 660° F.†, they unite and form water. If the resulting water be raised to a white heat, it is resolved into hydrogen and oxygen. Both metals (?) present the same phænomena.

* Athenæum, Sept. 19th, p. 966.

† Graham's Elements, 1st edit. p. 259.

At one temperature (nearly the same in both cases) combination with oxygen occurs; at a higher temperature, decomposition of the oxide happens. Many other examples might be given in illustration of the same fact. Such cases, however, do not seem to warrant a conclusion as to heat exhibiting anything like a polarity of force, by which I understand the manifestation in opposite directions of opposite powers of equal intensity. At all events, if the opposite effects of different *intensities* of the same agent be considered equivalent to a polarity of action, it is difficult to see what force may not be called a polar one. The decomposing and combining power of heat of different intensities, seems exactly comparable to the opposite effects of different intensities of mechanical impulse.

If two pieces of smooth glass are laid together and struck gently or compressed slightly, they unite or cohere. If the united pieces are thereafter exposed to a sharp blow or to great compression, the union is dissolved, or they are shattered to fragments. Here the same force effects mechanical synthesis and mechanical analysis. But in these contrasted actions, as seems to be the case also in Mr. Grove's experiments, the results are occasioned by a difference in degree of intensity of the same power, not as in the opposite effects of a polarizing force like electricity, by a difference in the kind of power which appears, whatever be its intensity. There is one form, indeed, of Mr. Grove's experiment which at first sight does not appear to admit of the explanation proposed in reference to the other trials—I allude to the decomposition of steam by the electric spark, which is well known to have the power of combining hydrogen and oxygen into water. A similar experiment was made in perhaps a still more instructive form in the latter part of last century by Beccaria*, Pearson and Van Troostwyk, and more recently by Wollaston†, in his well-known decompositions of water with guarded poles. In certain of these trials it was found that Leyden jar discharges sent through water, decomposed it till the accumulation of permanent gas left the wires bare; after which the first spark that passed recombined the gases into water, which again covered the wire, when decomposition could anew be obtained. Here, to appearance, the same agent acting with the same intensity, alternately decomposed and recomposed water. For argument's sake, let it be acknowledged that the heat alone of the spark was the cause of chemical change. Nevertheless it may be questioned, whether

* Lettere deli' Electrécismo, quoted in Lardner's Electricity, vol. i. p. 78.

† Faraday's Electrical Researches, series 3, paragraph 328.

it acted with equal intensity in both cases. The electric spark must be conceived, according to the results already given, to be at first at a high white heat, and whilst retaining this temperature we may believe it to possess a power of disuniting the elements of water, and of preventing their union. But as soon as the spark falls to the temperature of 660° F., it loses its power of decomposing water, and, on the other hand, acquires a power of uniting hydrogen and oxygen. Although therefore the spark is always *furnished* of the same intensity, its action may change, and even be reversed, as its intensity diminishes. Moreover, even when the spark is white-hot, it is only the amount of matter directly in its track that will be raised to a white heat. Contiguous portions will have their temperature much lower, so that in the case of hydrogen and oxygen, at some little distance from the route of the spark, the temperature will be 660° F., and there combination will begin, and ultimately extend through the whole mass of gas.

In like manner, when a platinum wire is made white-hot in a mixture of hydrogen and oxygen, it causes their combination. Here we may suppose that union occurs as soon as the temperature of the metal rises to 660° F., and before it acquires a white heat. Or if we were to arrange matters so that the wire should be made white-hot in a vacuum and hydrogen and oxygen afterwards admitted to it, still union of the gases should happen; for although the wire might prevent combination immediately around itself, at no great distance where the temperature was below 700° F. it would compel union. In all such experiments the combining effect of heat will be much more manifest than its decomposing power; not that perhaps the former is in reality greater than the latter, but because flame is propagated through a mixture of hydrogen and oxygen by a series of combustions. The hot wire or the electric spark kindles only the portions of gas immediately adjacent to it, but the combustion of those sets fire to the molecules contiguous to them, and these in their turn to their neighbours, till all are made to burn. Thus the flame travels after the original cause of combustion has ceased to operate directly, and the momentary action of a small spark, or the transient heat of a red-hot capillary wire may suffice to fire an infinitely large mass of hydrogen and oxygen. There is no provision for a similar propagation of decomposition through water or steam when either is made white-hot; the absolute amount accordingly of disunion of the elements of water occasioned is very small.

If allowance, however, be made for the apparent difference in extent of effect which heat shows in uniting and in dis-

uniting the elements of water, the phænomena otherwise seem referable solely to the intensity of the temperature to which hydrogen and oxygen are exposed. The opposite processes might go on simultaneously, union or disunion being determined simply by the different temperatures to which different portions of the gases were raised. At least it seems not improbable that if a mixture of steam and of hydrogen and oxygen were exposed to electric discharge, decomposition of the steam and combination of the hydrogen and oxygen might be effected by the same spark, provided the volume of steam were not large. In the track of the spark decomposition would occur, so long as a white heat prevailed. When the temperature fell, combination would happen where the spark had passed, if it had not already commenced in the neighbourhood of its direct route. Similar remarks apply *mutatis mutandis* to the action of a hot platinum wire on a mixture of steam with oxygen and hydrogen.

It may be objected to this view, that Mr. Grove decomposes steam in his eudiometer, and obtains a permanent bubble of gas, consisting of hydrogen and oxygen. The bubble however obtained in this way is very small, and could not probably be greatly increased. Mr. Grove has not mentioned how large a volume of hydrogen and oxygen he could obtain in the same eudiometer, by alternately boiling the water till the steam produced caused the liquid to fall below the wire, and allowing the steam to condense till the water rose above the metal. But I venture to say that no large volume of permanent gas could be procured by this process if the same eudiometer were employed many times successively. The combining action of the wire might not take effect on the hydrogen and oxygen when their quantity was small, and they were diluted through a large volume of steam, for in virtue of the law of diffusion, the molecules of hydrogen and oxygen would be separated from each other by molecules of water-vapour; but when the latter diminished in bulk, it seems impossible to doubt that kindling of the gases would occur.

Mr. Grove's experiments then do not appear to prove that heat of the same intensity is able in the same circumstances to form water and to decompose it. When therefore it is stated that water can be produced by the processes that disunite its elements, the word 'process' can only be understood to signify that the general arrangement in both cases is the same, not that the intensity of the agent called into play, or its mode of action is identical. If this could be affirmed, we should be able to announce as a general proposition, that

manifestations of the same force absolutely identical as to quality, quantity and intensity, could produce totally opposite results, which would be tantamount to affirming that unlike effects may flow from the same cause, without any alteration in the qualities or conditions of the latter.

The last observation I would make refers to the curious fact noticed by Mr. Grove, namely, that when a platinum wire is heated white-hot in steam, "in a few seconds a small bubble of gas is formed; but if the action be continued for a week, it does not increase in quantity*."

Are we to suppose that the wire is at the same time decomposing water around itself, and producing water at a little distance, undoing in one place what it effects in another, so that no permanent accumulation of gas is allowed to take place? This is possible, but I think not likely. The observation made by Mr. Grove seems sufficiently explicable, on the supposition that as soon as the wire is completely enveloped in steam, the thermo-circulatory currents which the high temperature occasions in the vapour prevent it from remaining long enough in contact with the wire to become heated white-hot. The steam probably circulates endlessly around the wire without a trace of decomposition occurring in it. It seems not unlikely indeed that in Mr. Grove's experiments with his eudiometer it was not steam that yielded the hydrogen and oxygen obtained, but the last film of water below the wire, which could not escape from the metal, but tended rather, in consequence of its expansion, to rise towards it, and was thus compelled to acquire a white heat, and to break up into its elements. If this view be correct, an arrangement where a white-hot wire or sheet of platinum foil was kept grazing the surface of water, might be found to effect a continuous decomposition of the liquid in question.

It is no objection to this view that an electric spark decomposes steam readily, for the duration of the spark is so short, that there is no time for the production of thermo-currents, nor any possibility of the steam escaping from the powerful topical action of the discharge. The spark may be compared to fulminating silver, whose action is instantaneous and violent, but quite local,—the heated platinum to gunpowder, the effect of which is cumulative and more general.

* Athenæum, Sept. 19th, 1846, p. 966.

March 30, 1847.—Anniversary Meeting.—The President in the Chair.

The following Report of the Council was read by the President, and subsequently ordered to be printed in the Society's Transactions :—

*Annual Report of the Council.*

IN reporting upon the progress of the Society during the past year, the sixth of its existence, the Council has still the satisfaction to mark an increase in the number of its contributing Members. It is now composed of 94 resident, 102 non-resident, 7 Foreign, and 6 Associate Members; giving an income of 290*l.*; the elections for the last year being 6 resident, 8 non-resident, 1 Foreign, and 2 Associate Members. Of the new ordinary Members, four have been received from the class of Associates. Conducted from the first on its present œconomical footing, without any salaried officer, or any of the expenses of an establishment beyond the moderate rent of 25*l.* per annum paid to the Society of Arts, the Chemical Society has been maintained by an annual average expenditure of about 180*l.*

No information of the loss of any of our Members by death has reached the Council since the last Anniversary.

Although an event not immediately connected with the Society, the Council has much pleasure in commemorating the late successful establishment in London of Chemical Laboratories, expressly designed to further the prosecution of original research. The new laboratories of the College of Chemistry, and of the two older colleges of the London University, now offer facilities for practical instruction and research not surpassed we believe in any foreign school. They already exhibit their efficiency, and claim our grateful recognition in the persons of new and promising contributors to our Memoirs.

The Council has also observed with interest that steps have been taken by the Royal Agricultural Society to obtain an extensive series of analyses of the ashes of plants. The exertions of two fully competent chemists, Messrs. Way and Ogston, have been secured by the Society for a period of two years, for that purpose.

Since last Report the Society has published Parts 17, 18, 19, and 20 (the last in course of issue) of their Memoirs and Proceedings. These comprise a continuation of their researches on Specific Gravity and Atomic Volume, by Messrs. Playfair and Joule, containing new determinations of a large series of the densities of metals, their oxides and sulphurets,

and several non-metallic elements, in different physical conditions, and illustrative of the allotropism and dimorphism of many of these bodies. The authors draw the inference from these as well as their preceding results, that the atomic volumes of bodies stand in a simple multiple relation to each other.—An elaborate paper by Mr. Griffin, on the Constitution of Aqueous Solutions of Acids and Alkalies, in which he finds that among several soluble bodies which he examined, only one (ammonia) had a fixed or nearly fixed volume in solution.—Experiments by Messrs. Playfair and Joule on the Temperature of Maximum Density in Water, which they fix by a new method at 39°·1 Fahr.—An examination of Palmic Acid, by Dr. Playfair.—Professor Redtenbacher on the Common Origin of a Class of Organic Acids, of the general formula $(CH)_n O_4$, which he has produced artificially by the oxidation of oleic acid. From the volatile products of that action he succeeded in separating nine different acids, having the expressed relation in composition, namely the acetic, metacetonic, butyric, valerianic, caproic, œnanthylic, caprylic, pelargonic and capric acids.—Drs. Muspratt and Hofmann on the Formation of Nitraniline, an interesting member of the aniline series, in which an equivalent of hydrogen is replaced by hyponitric acid ($NO_4$), as has already been done by chlorine and bromine by the same chemists, without the entire loss of basic power in the resulting compound.—An interesting discrimination and analysis of the various Blue Compounds of Cyanogen and Iron, by Dr. Williamson.—A continuation by Mr. Schunck of his researches on the Substances found in the *Roccella tinctoria*.—Researches on Cumarine, by Mr. Herman Bleibtreu.—An Account of the Compounds of Phosphoric Acid and Aniline, by Mr. E. C. Nicholson; and of the Metallic Metaphosphates, by Mr. Maddrell.—An investigation of the composition and properties of Gun-cotton by Messrs. Porrett and Teschemacher.—New Analyses of the Sulphites, by Dr. Muspratt.—A new, carefully executed Analysis of the Water of the Thermal Spring at Bath, by Messrs. Merck and Galloway; and a paper by Professors Wöhler and Liebig, on two new Artificial Organic Bases—Thialdine and Selenaldine; besides shorter communications of interest from Professor Schönbein, Dr. Ulex, Mr. John Wilson, Dr. Kolbe (two communications), Mr. Bowman, Dr. Fownes, Mr. Gladstone, Professor Graham, Mr. How, Mr. Sorby, Mr. Rowney, Dr. Smith (two communications), Mr. T. Taylor, Mr. Reekes, and Professor Liebig.

The Treasurer's Audited Account accompanies this Report.

# AUDITORS' REPORT.

*Dr.* ROBERT PORRETT (*Treasurer*), *in Account with the Chemical Society of London.* *Cr.*

| 1846. | | £ | s. | d. |
|---|---|---|---|---|
| March 26. | To Balance from last Account ..... | 442 | 0 | 10 |
| June 4. | — Proceeds from sale of Memoirs, &c. to 31st of December, 1845 ..... | 20 | 0 | 3 |
| 1847. March 19. | — Proceeds from sale of Memoirs, &c. to 31st of December, 1846 ..... | 7 | 16 | 2 |
| March 23. | — Subscriptions collected in the past year, including 1 Composition of £10..... | 220 | 0 | 0 |
| | | £689 | 17 | 3 |

| 1846. | | £ | s. | d. |
|---|---|---|---|---|
| May 22. | By payment of bill for Printing, &c. to November 1845 ..... | 132 | 19 | 5 |
| June 13. | ———— for Printed Receipt Book, 1846..... | 0 | 8 | 9 |
| 13. | ———— to Collector for Poundage & Postage | 8 | 10 | 3 |
| 30. | ———— Postage Stamps for Treasurer ..... | 0 | 1 | 0 |
| July 27. | ———— to Society of Arts for Rent..... | 25 | 0 | 0 |
| Dec. 24. | ———— to Servant and Doorkeeper at Society of Arts, 10*s.* each ..... | 1 | 10 | 0 |
| 24. | ———— to W. Stacey for Tea and Coffee ... | 9 | 14 | 0 |
| 1847. March 5. | ———— to D. Nutt for Books ..... | 3 | 8 | 0 |
| 19. | ———— to R. and J. E. Taylor for Books ... | 2 | 7 | 0 |
| 19. | ———— to R. and J. E. Taylor for Printing, &c. to November 1846..... | 115 | 13 | 10 |
| 19. | ———— to H. Baillière for Books to this date ..... | 10 | 12 | 6 |
| 19. | ———— to A. Crawford for Bookbinding to November 1845 ..... | 2 | 10 | 4 |
| 23. | By Balance carried to his Debit in new Account . | 377 | 2 | 3 |
| | | £689 | 17 | 3 |

We have examined the above Accounts and find the same correct,

PHILIP J. CHABOT,
CHARLES DAVY, } *Auditors.*

London, 23rd March, 1847.

London, 23rd March, 1847.

(Errors excepted) R. PORRETT,
*Treasurer to the Chemical Society.*

The Society then proceeded to the election of Officers and Council for the ensuing year, when the following gentlemen were declared duly elected:—

*President.*—William Thomas Brande, Esq.

*Vice-Presidents.*—Arthur Aikin, Esq., Thomas Graham, Esq., John Thomas Cooper, Esq., Richard Phillips, Esq.

*Secretaries.*—Robert Warington, Esq., George Fownes, Ph.D.

*Foreign Secretary.*—A. W. Hofmann, Ph.D.

*Treasurer.*—Robert Porrett, Esq.

*Council.*—Walter Crum, Esq.; Warren De la Rue, Esq.; Sir Robert Kane, M.D.; W. A. Miller, M.D.; Jonathan Pereira, M.D.; Lyon Playfair, Ph.D.; Maurice Scanlan, Esq.; Edward Schunck, Ph.D.; John Stenhouse, Ph.D.; E. F. Teschemacher, Esq.; James L. Wheeler, Esq.; Lieut.-Col. Ph. Yorke, R.E.

The thanks of the Society were voted severally to the President, Officers and Council for their services during the past year.

It was moved by Dr. L. Playfair and resolved,—"That the Council be requested to take into consideration whether means can be devised for a more regular and efficient publication of the Memoirs presented to the Society."

The Society adjourned to April 5th.

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April 5, 1847.—Thomas Graham, Esq., Vice-President, in the Chair.

"On the Chemical Composition of Calcareous Corals, by J. Silliman, Jun., Esq.," was presented by the author, with several copies for distribution.

The following papers were read:—

On a Modification of the Apparatus of Varrentrapp and Will for the estimation of Nitrogen. By Warren De la Rue, Esq.

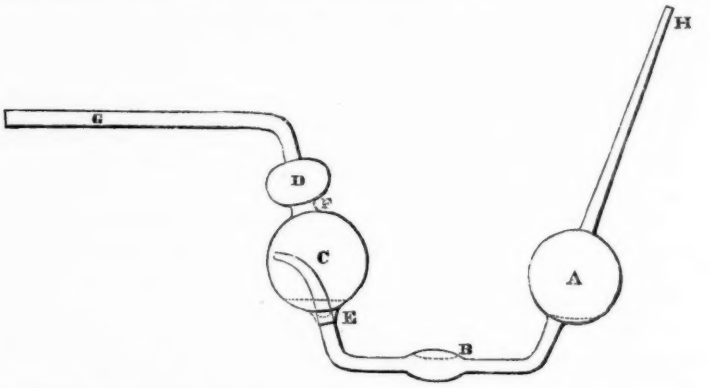
My attention having been called to a communication by Mr. Alex. Kemp in the number of the 'Chemical Gazette' for the 1st of April 1847, in which he describes a modification of Messrs. Varrentrapp and Will's tube for nitrogen determinations, of a very similar construction to one I employed as far back as November 1845 in the laboratory of the Royal College of Chemistry, and which I have repeatedly shown to my friends, I am induced to lay before the Society a description of my form of apparatus, which differs somewhat from that described by Mr. Kemp.

By the drawing, it will be seen that the tube B E, instead of opening immediately into the bottom of the flattened bulb C, is prolonged and rises for some distance into the bulb curving over towards its side; in this respect Mr. Kemp's apparatus does not differ materially from mine. I found it necessary however to have a third bulb (D) blown (which is best of a spheroidal form), in order to effectually prevent the acid from being drawn into the tube G whenever a sudden absorption took place; this third bulb communicates with C by a narrow neck. If the apparatus be constructed without

the third bulb D, a portion of fluid generally passes into the tube G from the rotary motion induced in the fluid in C.

The dotted lines indicate the height of fluid in the bulbs, and this quantity is quite sufficient for the condensation of all the ammonia likely to be formed. I would remark, that if during the progress of the combustion a cessation of the production of gas should occur, the construction of the apparatus is such as to prevent the whole of the acid ever being carried over into the bulb C, so that on the evolution again commencing no fear need be entertained for the complete condensation of the ammonia.

It only remains for me to add, that though this new form of apparatus is not so readily rinsed out as the original one of Messrs. Varrentrapp and Will, no great inconvenience is experienced from that cause, as the acid can, at the close of the operation, be easily caused to flow into the bulb C and out at the tube G, by properly inclining the bulbs, &c., and when this is done water or alcohol may be introduced by a pipette through the limb H.




## CXCIII. *On Transformations produced by Catalytic Bodies.* *By* Lyon Playfair, *Esq.*

BERZELIUS rendered a most useful work to science, when he collected into one class those varied phænomena of chemical action resulting from causes certainly very different from the ordinary manifestations of those affinities, which produce combinations or promote decompositions. This philosopher believes the power *, which causes decomposition without the acting body participating in its result, to be a distinct electro-chemical agency different from other recognised powers, and he named it the "Catalytic force." According to this view, catalytic bodies do not act by chemical affinity, but they excite inherent affinities in other substances,

* *Jahres Bericht*, xv. 237.

in consequence of which new combinations or decompositions ensue.

Mitscherlich *, adopting this view, considered a number of catalytic decompositions in detail, and showed the important influence exerted by the state of surface of bodies in favouring this peculiar action, which he denominates decomposition by *contact*. The examples, adduced in this interesting memoir, of the favourable action of an extended surface upon combination, fully prove that the physical condition of bodies exercises an important influence upon the action of this force; but they do not remove the necessity for studying the force itself, as it may either be a *vis occulta*, entirely distinct from powers already recognised, as Berzelius supposes, or may be modified forms of those in continual operation.

Liebig† views the catalytic power as a dynamical action on the atoms of a complex molecule, conceiving that the activity of the atoms of a body in a state of motion may be communicated to those of another body in a state of rest. The atoms of a compound, according to this view, if in a state of exact statical equilibrium, arrange themselves according to new affinities, when the *vis inertiæ* is overcome by motion. In proof of this view, Liebig carefully examines a large number of decompositions, and accounts for some of the most difficult transformations in organic chemistry.

But there are many instances, to which I shall have to draw attention in the present memoir, where catalytic decompositions ensue when there is no intestine motion in the atoms of the exciting body; and hence we cannot do more than consider motion as favourable to the development of dormant affinities, in a manner similar to the surface action described by Mitscherlich. The power of peroxide of hydrogen and of pyruvic acid to reduce oxide of silver is certainly a singular phænomenon, and appears favourable to Liebig's views; but the cause of the original decomposition of the peroxide of hydrogen cannot be ascribed to motion, as the atoms of the oxide of silver are not in that state, and those of the peroxide of hydrogen either not at all or only slightly so. Neither will it suffice to suppose that the escape of gas during such decompositions is due to the presentation of angular points from which the gas may escape ‡, because solutions of alkalies equally effect the decomposition, according to Thenard §. The cause, therefore, which enables cer-

* Taylor's Scientific Memoirs, or Pogg. *Ann.* xxxi. 281.
† Liebig's Chem. of Agriculture, 4th edit., p. 284.
‡ *Ann. der Pharm.*, ii. 22.
§ *Ann. de Chim. et de Phys.*, xlviii. 79.

tain substances to hasten the decomposition of such bodies as peroxide of hydrogen or persulphuret of hydrogen, although favoured by the state of surface and by motion, is independent of mere physical condition.

In further proof of the importance of motion in causing combination or decomposition, Liebig cites the favourable effects of agitation on the precipitation of potash by tartaric acid. It may be questioned, however, whether this is not either a mechanical breaking up of a combination or the simple effect of cohesion. Thus when water is saturated with a gas, a brisk agitation with a rod causes the separation of bubbles of gas previously dissolved. The mechanical force may here be supposed to have broken up the compound molecule of water and gas by detaching the former, and thus enabling the gas to escape by its elasticity. In the precipitation of potash by tartaric acid, cohesion may effect the same result that elasticity does in the case of gas, the agitation knocking off the atoms of water which are feebly attached. In fact we know that the addition of alcohol equally aids the precipitation, the action here being a chemical separation of the water, as in the other it is mechanical. The diminished solubility of the salt, after it has been influenced by cohesion and separated from water, has its counterpart in many similar instances; for example, in the small solubility of anhydrous sulphate of iron. The effect of agitation on a solution of sulphate of soda, saturated while hot and allowed to cool, I ascribe to the same cause. The supposed effect of cohesion or elasticity in these cases is nothing more than that constantly observed in ordinary phænomena, when the gravity of a substance is different from that of the medium in which it exists. The vesicles of water in the atmosphere may be so small that they float in it and produce fogs; but when aggregated together by the motion of the air, they form drops, which precipitate to the ground with a rapidity proportionate to their size: the converse of this is also true. Thus, the particles or aggregated atoms of carbonic acid in water may be so very small, that, with the slight affinity of the latter added, they may be enabled, when in a state of rest, to remain without resuming their elastic form; but agitation causes a larger system of aggregated atoms, and the gas now escapes in small bubbles.

The first instance of cohesion applies in the precipitation of tartar. At the moment of formation the particles may be so widely apart, that, aided by their slight affinity for water, they remain without aggregating to any considerable extent. Brisk agitation, and the presentation of an extended surface,

effect their aggregation and cause a speedy precipitation. It may be that these are really instances of combination favoured by motion; but presuming that they are, the general argument is not affected, that other decompositions perfectly analogous are produced where the exciting body is in a state of rest.

The third theory of these decompositions is, that catalytic bodies act by exerting a feeble chemical affinity on one of the constituents of the body decomposed. This view was introduced by Mercer *, and supported by several very ingenious experiments communicated to the British Association at its meeting in Manchester. One of these was, that protoxide of manganese had the singular power of hastening the oxidation of starch in nitric acid †. The metallic protoxide, from its disposition to pass into the state of peroxide, aids the oxalic acid to decompose the nitric acid, the united affinities of both being able to accomplish what neither by itself could do. The protoxide remains unaffected at the end of the experiment, because, under the circumstances (the presence of acid), it cannot gratify its desire to become peroxide, and, therefore, it passes over its oxygen to the carbon, which escapes as carbonic acid. Mercer cited, as further examples, the action of protoxide of copper in eliminating oxygen from a solution of hypochlorite of lime, and of peroxide or binoxide of nitrogen in commencing the oxidation of a mixture of protochloride of tin and nitric acid. Mercer implied by these instances, that catalysis is an affinity of the catalytic agent for an element in the body acted upon, that affinity being feeble and incapable of gratification under the circumstances.

It would be advantageous to science if we could arrange under a known power the cases of decomposition which appeared so mysterious as to induce the great Berzelius to ascribe them to the action of a new force. It may not be possible in the present state of our knowledge to comprehend the whole of the instances observed, but, if most are included in one category, we have a right to suppose that the others may be embraced as our knowledge progresses. I shall therefore endeavour to show that many catalytic decompositions are

* Reports of British Association, vol. xi. 2d Part, p. 32.

† The experiment is easily made by dissolving 1 ounce oxalic acid in $\frac{1}{7}$ a pint of water at 180° F., and adding to this 1 oz. colourless nitric acid of 1·30 sp. gr. No action ensues on this mixture, but it immediately commences on the addition of a protosalt of manganese, which for simplicity may be the oxalate or nitrate. The action is also strikingly shown by heating a mixture of oxalic acid until the action commences, then diluting it till all action ceases. A little protosalt of manganese now added to the solution causes an immediate renewal of the oxidation.

merely cases of chemical affinity exerted under peculiar conditions.

In no instance of chemical union does there seem to be such a complete gratification of affinity as to suppress the attractions of the elements. The inherent affinities still remain more or less powerful, for, if it were not so, the compound would be permanent under all circumstances and not liable to further change by the action of external agents. When manganese unites with 1 atom of oxygen, the affinity of the metal for oxygen is not wholly merged, but is still strong enough to attach to itself 1, 2 or 3 atoms more oxygen. When the oxide is one of the lowest of the series, this affinity exhibits itself in a *basic* power by attaching itself to any complex highly oxygenized molecule, such as the oxygen acids, or of radicals playing the part of oxygen. When, on the other hand, the manganese or other radical becomes highly oxygenized, we find it possessing *acid* properties, that is, the additional atoms of oxygen, being less firmly attached, are capable of gratifying the disposition of a less oxygenized atom (the base) to attach itself to a higher oxide, or, to use the convenient phraseology of Graham, the base becomes zincous to the acid, which is now chlorous.

On heating the nitrates, nitric acid is not given off, but $NO_4+O$. The decomposition readily results from the disposition of the base to appropriate more oxygen and pass into the higher oxides. If the base be oxide of nickel, the oxygen becomes attached to the oxide and remains; if, however, an oxide which has but a feeble affinity for oxygen at an elevated temperature, the elasticity of that element is able to overcome the affinity, which succeeded in breaking up the nitric acid. The final action is so obviously dependent upon the oxygenous part of the acid, as to make Schönbein believe that salts contain peroxides ready-formed; thus that $NO_5$, $HO=NO_4+HO_2$, or PbO, $NO_5=NO_4+PbO_2$. This however is an unnecessary supposition, the previous view accounting sufficiently for the decomposition of a nitrate, so as to produce $NO_4$ and O. Admitting this view to be correct in the expression that the preponderating quantity of a chlorous element in an acid renders the latter chlorous to a base, the mechanical attachment being to the chlorous element, we can understand why the number of atoms of oxygen in a base should regulate the number of atoms of acid attached to it. Thus RO presents only one chlorous element of attachment to the acid, and therefore the latter adheres to it in one proportion; whereas $R_2O_3$, which possesses three atoms of a chlorous element equally distributed

round a zincous nucleus, presents three points of attachment, and therefore produces a salt $R_2 O_3, 3A$. This view in result gives all the simplicity of the acid radical theory, both views entertaining the idea that the oxygenous atoms of the base and acid are attached to each other. We have certain instances, as for example $KO, ClO_5$; $PbO, NO_5$, where the elastic atoms of oxygen combine as closely together as non-elastic atoms, such as lead or silver.

Although to aid conception we may suppose the atoms of oxygen of the base and of the acid to be in mechanical connexion, the true arrangement is probably not so, seeing that in a base there is always a part more zincous than the oxygenous atom, although the base as unity is zincous to the acid. We see many instances in chemistry of union of atoms in *pairs*, or what may be called *dual affinity*. This Graham* has proved to be the case with regard to atoms of water, and we know of numberless instances in the case of oxides. Thus RO uniting with oxygen forms $RO_2$. In this case RO + O corresponds to RO + A, the acid here representing the chlorous element from its oxygenous character. It is not necessary to suppose that A and O are associated in one continuous line, the probability being that the molecule may really be represented by ARO. Thus also in $R_2 O_3$, where the $O_3$ are probably grouped equally round $R_2$, there is room for three more of a chlorous element to gratify the dual affinity, and the general formula $R_2 O_3, 3A$ is the result, the 3A here representing three of a simple chlorous element. The result, as regards affinity, will still however be the same, the whole depending upon the attraction of the central nucleus R. It is therefore only for simplicity of expression in studying the phænomena of catalysis, that I view the atoms of oxygen of an acid as associated in mechanical continuation with the atoms of oxygen of the base, the *effect* being represented by this expression: the whole views of molecular or atomic constitution of bodies are in my opinion only convenient fictions to enable us to study the forces themselves, and the conception of a mechanical arrangement I only adopt as expressive of the manifestations of powers residing in matter.

To show that the tendency of bases to $NO_5$, even without being combined, is to attach themselves to the oxygenous part of the acid, a curious phænomenon observed by Mercer may be cited.

A portion of alumina may be taken and placed at the bottom of a vessel containing warm $NO_5$; no action ensues, ex-

* Trans. Royal Soc. Edin. vol. xiii.; Phil. Trans. 1837, p. 47 *et seq.*; Memoirs of Chemical Society, vol. ii. p. 51 *et seq.*

cept partial solution; a slip of calico coloured in indigo-blue may now be introduced into the mixture, and remains unaffected in the clear acid, but is immediately discharged when pressed with a glass rod into the alumina. Here the alumina acts by placing the oxygen of the nitric acid in a state of tension without however succeeding in decomposing it, but the moment an assistant affinity comes into play, that state is shown by the decomposition of the nitric acid and oxidation of the indigo. The alumina in the presence of the acid could not oxidize (in fact, we know of no higher oxide), and therefore the indigo appropriates the oxygen. I find that various other oxides, such as calcined $Cr_2 O_3$ and $SnO_2$, have the same power, the latter showing this disposition more strongly than any of the other oxides. The best mode of trying these experiments is to heat a certain quantity of nitric acid, and then dilute it till indigo cloth ceases to be bleached. The oxide of tin is now added and allowed to fall to the bottom. On introducing a slip of indigo-blue calico, the portion in the clear acid will be found to remain unaffected, while that in contact with the insoluble oxide will be bleached in a few seconds. That this decoloration of the indigo is due to the assistant affinity of another body acting in the same direction, *i. e.* also having a disposition to unite with oxygen, may perhaps best be shown by the following experiment:—Warm nitric acid is diluted to such extent that it just ceases to discharge indigo-blue calico; it is then divided into two portions, with slips of coloured calico in each, and through one of these binoxide of nitrogen is passed. In the latter the indigo becomes quickly bleached, while it remains unaffected in the former, the action obviously being due to the accessory affinity of the nitric oxide for more oxygen. In the same way indigo-blue is discharged during the decomposition of a nitrate by heat, other kinds of organic matter being oxidized under like circumstances; in these instances the decomposition of the nitric acid is much facilitated,—1. by the affinity of the base for oxygen; 2. the affinity of the organic matter for oxygen, which unites with it at the elevated temperature. There are many similar instances of this kind, where the behaviour of $NO_2$ or $NO_4$ as an assistant is too clearly contrasted with the action of other bodies to permit mistake. Thus urine when kept is unfit for the preparation of urea, that substance having been converted into carbonate of ammonia during the action of the air upon the mucus or colouring matter contained in the fluid. Colourless nitric acid unites with urea and may be heated with it without decomposition; but nitric acid containing any of the lower oxides of nitrogen, such as

$NO_2$ or $NO_4$, immediately decomposes urea into carbonic acid and ammonia*. We cannot conceive that a lower oxide can more readily oxidate urea than a higher oxide, and hence we can only view the $NO_4$ as aiding the urea to oxidize itself, as the mucus does in urine. In the same way, the action of pure nitric acid on colourless uric acid is to form alloxan, if the operation has been conducted so as to prevent the formation of nitrous acid ($NO_4$) during the oxidation. But if $NO_4$ has been evolved, or if the colouring matter of the urine be still contained in the uric acid, the products are only carbonate and oxalate of ammonia. The colouring matter of the urine and $NO_4$ are thus seen to possess a similar action, which is exactly the same as that of protonitrate of manganese on a mixture of starch and nitric acid, no oxalic acid being formed in the presence of this salt, the only product of oxidation being carbonic acid. The $NO_4$ or $NO_2$ acts in these cases clearly by aiding the compound ready to oxygenate, but which, under the conditions, has not sufficient power to decompose the nitric acid without additional aid. The same explanation probably applies to the singular discovery of Professor Graham†, that the addition of $NO_4$ to non-accendible phosphuretted hydrogen renders it inflammable. In this case the two combined affinities produce the union of oxygen with one of the bodies. The presence of the small quantity of another compound of phosphuretted hydrogen in the spontaneously accendible gas, as described by Leverrier‡ and by Thenard§, may probably act in the same manner.

The action of this compound ($PH_2$) corresponding to amidogen ($NH_2$) may be conceived so to disturb the attraction of the phosphorus to the hydrogen in the gas $PH_3$ as to produce the inflammability. Both the elements of this gas are highly combustible, uniting with oxygen at a low temperature. Their mutual attractions are sufficiently strong to prevent the oxygen breaking up this union; but when the second body is present, the desire of $PH_2$ for another atom of hydrogen may be supposed so far to draw the third atom of hydrogen from the $PH_3$, that oxygen has now the power to unite with the two inflammable elements. In disturbing the existing equilibrium, it is presumed to act just as a spark would do by elevating the already strong affinities of the two elements for

* A solution of urea in nitric acid is immediately decomposed with lively effervescence when a little $NO_2$ is passed through it.

† Trans. Royal Soc. Edin. vol. xiii. p. 5.

‡ *Ann. de Ch. et de Phys.* lx. 174.

§ *Comptes Rendus des Séances de l'Académie des Scences,* t. xviii. pp. 252, 914; t. xix. p. 313.

oxygen. When a solution of hypochlorite of lime is poured into a solution of muriate of ammonia in excess, a very pungent volatile compound results, which has no bleaching properties, and therefore does not contain hypochlorous acid. The decomposition is expressed by the equation $NH_4Cl + CaO, ClO = NH_2Cl + 2HO + CaCl$. The volatile compound $NH_2Cl$ has an affinity for hydrogen in order to pass into $NH_4Cl$. This body was well-fitted to test the view of the cause of the inflammability of phosphuretted hydrogen (even supposing $PH_2$ is not spontaneously inflammable, as it is stated to be by Thenard). On placing gas (which had entirely lost its inflammability by standing several days over water), in contact with the above mixture, in about an hour it acquired the property of smoking strongly in the air, although it did not inflame spontaneously. This showed that the affinity of $PH_3$ for oxygen was much elevated, although the attraction was not sufficient for inflammation.

There cannot be any doubt that the atoms of a body may be placed in a greater or less degree of tension by varying conditions. The experiments of Mr. Joule* and myself on Allotropism have fully proved that the space occupied by the same body alters under different circumstances. It is therefore not an unreasonable assumption that the affinity of one body for a particular element may be sufficiently great to produce a tense state of the atoms without effecting decomposition†: hence the added affinity of a second body acting in the same direction may cause that change which each alone could not effect. Anything that disturbs the state of statical equilibrium in such a body will often effect its decomposition.

This accessory affinity is recognised when both bodies enter into union. Charcoal and chlorine decompose alumina at a red heat, though neither can do so separately. In the same way Boudault‡ has shown that a mixture of potash or soda and red prussiate of potash oxidizes various metallic oxides, while Mercer has for many years made use

* Memoirs of Chemical Society, vol. iii. p. 93.

† The alteration in volume is best seen in those oxides which contract and increase in specific gravity by the application of heat, for example, when the brown oxide becomes the green oxide of chromium. The two oxides must have a different molecular constitution, and this may be supposed to result from the elastic powers of one of its elements and the cohesive force of the other. The first effect of heat on oxide of chromium must be to expand the atoms of oxygen, and removing them further from the two atoms of chromium, permit the cohesive attraction of the latter to be gratified. Hence the compound acquires properties dependent upon cohesion, such as indifference to union and diminished solubility.

‡ *Journal de Pharmacie*, tome vii. 437.

of this mixture to discharge indigo-blue on calico*. Red prussiate of potash ($Fe_2 Cy_6 3K$) has a great disposition to attach to itself another atom of potassium to become yellow prussiate of potash ($Fe_2 Cy_6 4K$). It cannot gratify this desire without aid; but when assisted by a substance having an affinity for the oxygen of the potash, and capable of appropriating it, decomposition follows. There are often cases in which the body exercising the accessory affinity may be unable to effect the union, either by the influence of unfavourable chemical conditions or of cohesion or elasticity. Thus, in the case with which we first started, the affinity of protoxide of manganese for oxygen aids in the decomposition of nitrate of protoxide of manganese, and sesquioxide of manganese remains. If the temperature during the decomposition be elevated, the oxygen resumes its elastic state and refuses to form this higher oxide, as in fact we know is the case in Mercer's experiment with oxalic acid and nitric acid, where the presence of hot $NO_5$ is an unfavourable chemical condition to the existence of $Mn_2 O_3$, and therefore it is not formed, but in its stead the oxygen is passed over to the organic matter, which is able to unite with it under the circumstances. A similar instance of the effect of such conditions is seen when the peroxides of copper, manganese or lead, are thrown into a solution of bleaching powder. The affinity of these oxides for an additional quantity of oxygen enables them to decompose the hypochlorite of lime, converting it into chloride of calcium. When the protoxides are used, this liberated oxygen unites and converts them to peroxides. The latter themselves have sufficiently strong affinity for oxygen to cause the decomposition to proceed; but not uniting with it, pure oxygen is given off in the gaseous state. Here elasticity has come into play, and being more powerful than the feeble chemical affinity, causes the oxygen to escape as a gas. When the solution is cool the gas goes off in a succession of small bubbles; but when hot, the escape is tumultuous, the heat aiding the oxygen to enter into the elastic state†. A solution

* Memoirs of the Chemical Society, vol. iii. p. 320. In justice to Mercer, although this does not remove Boudault's claim of priority of publication, I cannot refrain from stating that the former chemist pointed out to me the oxidizing powers of the prussiates four or five years since.

† The best mode of instituting the experiment is to make a mixture of chloride of soda and caustic soda, heat this to a temperature near ebullition, and add sulphate of copper. The oxide of copper precipitated in the fine state of division causes such a copious evolution of oxygen gas that the contents are apt to be thrown out of the vessel: a mixture of chloride of lime and lime, or the ordinary unfiltered bleaching-powder of commerce, are also well-fitted to show the action.

of chloride of lime evolves oxygen slowly at the boiling-point; but the decomposition is much accelerated by the accessory agents referred to.

The action of certain oxides upon peroxide of hydrogen is exactly similar to that on a solution of hypochlorite of lime. Thus peroxide of manganese, the protoxides of cobalt and lead, minium, peroxide of iron, and the protoxides of nickel, copper and bismuth, all exert this action on peroxide of hydrogen with a force indicated by their order*. In none of these cases does the oxide unite with a further proportion of oxygen. The violence of the action is however in proportion to their power of uniting with more oxygen. The first five oxides in the list have higher oxides of definite composition and of a certain degree of stability, with the exception of ferric acid; while the protoxides of copper and bismuth, although possessing the power of uniting with more oxygen, do not present superior oxides of a marked character. We should have expected the oxides of nickel and cobalt to have exerted the same power, but from Thenard's description of the former being in the state of a black powder, it may have been the oxide of increased specific gravity, to which attention has already been drawn†. In all these cases the affinity is supposed to be sufficiently strong to break up the atoms of a body yielding to the slightest disturbance of its state of statical equilibrium. Two affinities are at play in these decompositions, viz. the attraction of the metallic oxide for oxygen and that of the water for the same body; both these affinities resist the union, and therefore, elasticity coming into operation, robs both oxides of the gas. The affinity causing the decomposition is so slightly preponderating in its influence, that a second cause coming into operation is quite sufficient to alter the conditions under which it was originally exerted, and to draw one of the elements of the body acted upon beyond the sphere of its affinity.

The balance of affinities in all such cases is so near that we not unfrequently find apparently contradictory effects resulting from their gratification. Thus the addition of oxide of silver to peroxide of hydrogen expels oxygen from the latter, but at the same time it is robbed of its own oxygen and reduced to the metallic state. In this case we have two feeble compounds instead of one, with affinities very nearly balanced, and with atoms so tense as to yield readily to the first disturbing cause. We can scarcely adopt as sufficient the ex-

* Thenard's *Traité de Chémie*, 6th edit. vol. i. p. 216.

† Memoirs of the Chemical Society, vol. ii. p. 384, and vol. iii. p. 81.

planation of Thenard and Mitscherlich*, that the reduction is due to the elevation of temperature accompanying the decomposition, because even when that is lowered by the addition of much water to the peroxide of hydrogen, the silver still becomes metallic.

It is a point yet undetermined, whether a lower oxide is to be considered as unity to a higher oxide, or whether all the atoms of oxygen are held by equal attractions. We know that tartaric acid is able to separate potash from nitric acid in forming a bitartrate, and yet acetic acid is sufficient to remove the second atom of potash from the neutral tartrate. But in a bibasic acid, like tartaric acid, it may be either atom of potash that is abstracted, and the superior affinity for the remaining one may be owing to attractions resulting after the expulsion of the first. Thus $MnO_2$ may have its atoms of oxygen distributed round the central nucleus Mn, and held by equal attractions, and the stability of the red oxide produced by its calcination does not show that it pre-existed in the black oxide, but merely that the attraction became stronger when one of the elements which divided it was removed. If it be admitted that the attraction of a radical for oxygen is equally divided between all the atoms of that element associated with it, the action to which we have alluded becomes comprehensible. In an oxide we have the attraction of affinity opposed by the elasticity of its oxygen and by the cohesive force of the metal. If $a$ be the attraction of the central nucleus or radical, $c$ the cohesive force of the metal, and $e$ the elasticity of the oxygen, then the molecular formula of a protoxide will be $\frac{a}{c+e}$, of a sesquioxide $\frac{2a}{2c+3e}$, and of a binoxide $\frac{a}{c+2e}$. Now if, as in oxide of silver, the $a$ and $e$ are nearly equal, or the $a$ only slightly preponderating, and the $c$ or cohesive force very powerful, we can readily conceive that the added force of a second $e$ may overcome the small amount of preponderating force in favour of $a$. Thus, when oxide of silver is placed in contact with peroxide of hydrogen, its affinity for more oxygen is sufficient to draw the second atom of oxygen beyond the sphere of attraction of H, and deliver it over to its own elasticity. But in doing this the attraction of silver for oxygen has been divided between its own oxygen and that of the peroxide of hydrogen. Scarcely at any time capable of retaining its own oxygen, this division of its attractive force has been fatal to the existence of its oxide, and the water *in statu nascens* at the same

* Poggendorff's *Annalen*, lv. 321.

time exerting an affinity for the oxygen just ready to escape; all these causes combined result in the reduction of the silver*.

When pyruvic acid is in contact with oxide of silver, it unites and forms a salt; but when acting on carbonate of silver, a certain quantity of oxygen also leaves the oxide during the escape of carbonic acid, and metallic silver remains†. As Liebig‡ suggests, motion may aid this result; but were this the only explanation, we should expect that silver would constantly be reduced during the action of other feeble acids on carbonate of silver. If, however, we suppose that the pyruvic acid, $C_6 H_6 O_5$, from its affinity for more oxygen, exerts an attraction for that element at the moment of the liberation of the carbonic acid, the decomposition would be similar to those we have already considered, especially if the previous view of the molecular constitution of salts be admitted. In that case the oxygen of the oxide being attached to that of the carbonic acid, will be made highly tense during the escape of the latter, and may therefore be detached by a very feeble force, its elasticity finally overcoming the weak affinity. An extension of the explanation however strikes me as more probable, but it would be premature to insist upon it without being supported by experiments which I have not yet been able to conclude.

The action of metals and of charcoal on peroxide of hydrogen may be explained by the same feeble affinity. Alkalies also, from their attraction for oxygen, as indicated both by their capability of uniting with more oxygen and by their basic power or disposition to attach themselves to a compound behaving as an oxygenous or chlorous element, favour the decomposition of $HO_2$, while acids, on the other hand, render it more stable, perhaps, as Thenard himself suspected§, from there being an inferior oxide ($H_2 O_3$?). In this instance the elasticity of the oxygen tends to conceal the play of affinities by preventing combination.

* During the passage of this paper through the press, Mr. Brodie, in a lecture at the Royal Institution, showed that peroxide of potassium reduces chloride of silver, the two atoms of oxygen passing off in the gaseous state, while chloride of potassium and metallic silver remain behind, a singular decomposition, when the behaviour of potash is remembered. But the action is strictly the same as that here described; the atoms of oxygen, being liberated at the same time, are presented to the silver, which, dividing its attractive force between them, is not able to overcome the influence of elasticity of the oxygen and its own cohesion, and therefore remains in a metallic state.

† Berzelius, *Lehrbuch der Chemie*, v. Auf. Band iv. S. 231.

‡ Chemistry of Agriculture, 4th edit., page 283.

§ *Traité de Chémie*, p. 211.

When the acting body is present in large quantity, or exhibits an increased surface, the action goes on with proportionate rapidity. Thus, when nitric acid is in contact with starch, the action is moderate until a certain quantity of peroxide of nitrogen has been evolved by decomposition, after which it proceeds with a violence difficult to control. The peroxide of nitrogen surrounding every particle of starch aids it in the decomposition of the nitric acid. That this is the real cause of the phænomenon may be proved by the following simple experiment. Nitric acid is heated with starch to a temperature at which the action has a tendency to commence but has not yet begun. A stream of $NO_4$ or $NO_2$ is then passed through the liquid, when action immediately begins with an activity proportionate to the quantity of gas added. The elevation of temperature due to the progressive action influences the decomposition, by causing the atoms of nitric acid to become more tense. Exactly the same accessory affinity is used by the manufacturer of oxymuriate of tin, when he adds a fragment of tin to the mixture of chloride of tin and nitric acid. The tin eliminating some nitric oxide quickens the action, which commences with difficulty with pure nitric acid; nitric oxide gas passed through the solution answers the same purpose.

This accessory affinity also enables oxide of copper or peroxide of manganese to evolve copious streams of oxygen from chlorate of potash in a state of fusion. The heat of fusion decomposes the compound slowly, but on adding a body having an affinity for the element acted upon by the heat (oxygen), the decomposition proceeds with greatly increased rapidity. We cannot ascribe this action to the presentation of points from which the gas may escape, as in the lowering of the temperature of ebullition by particles of sand, because silica has no influence in accelerating this decomposition*.

In the examples previously given we have the decompositions aided by the tendency of one of the bodies to assume the elastic form. But when the body acted upon has two elements, one of which is influenced by elasticity, the other by cohesion, we find it peculiarly liable to be acted upon by external agents. Persulphuret of hydrogen is a compound of this class, and has been closely studied in its decompositions by Thenard†. The same bodies which decompose peroxide of hydrogen act catalytically upon this sulphuret. The decomposition cannot be due to points for the escape of gas, as suggested by Liebig‡, to explain the decomposition of peroxide of hydrogen, because solutions of the alkalies act with

* Taylor's Scientific Memoirs, vol. iv. p. 9.

† *Ann. de Ch. et de Ph.* xlviii. 79. ‡ *Ann. der Pharm.* ii. 22.

equal power. The sulphurets, especially those of the alkaline metals, decompose it very readily. As in the case of peroxide of hydrogen, the acids afford stability to its sulphur analogue. In the view of acids given, they are supposed to have become chlorous or electro-negative, representing and behaving as oxygen, and therefore exerting no affinity, we should anticipate that they would not show any disposition to break up an oxygenous compound or its analogue of sulphur. Another instance of accessory affinity is seen in the nitrosulphates*; the formula ($RO, SO_2 + NO_2$) given by Pelouze to these compounds does not allow us to understand their decompositions, which however becomes intelligible if we view nitrosulphuric acid as nitric acid, in which the fifth atom of oxygen has been replaced by one of sulphur ($RO, NO_4 S$). In this acid we have two elements—the nitrogen and and the sulphur—sharing the oxygen, their mutual affinities being nearly balanced when the acid is united with an alkali, although in a free state, the sulphur exhibits a superior affinity, as shown by the decomposition which then results, $NO_4S = NO + SO_3$. Now any substance which acts as an accessory to the sulphur by aiding the withdrawal of oxygen from the nitrogen decomposes it. This instability is especially exhibited in $NH_4O, NO_4S$; the 3 atoms of hydrogen of the ammonia in their attraction for oxygen introducing another affinity, which accelerates decomposition. And, in fact, we do find that the same agents which so readily decompose the oxygenous compounds, chloride of lime and peroxide of hydrogen, do equally cause the disruption of nitrosulphate of ammonia into protoxide of nitrogen and sulphate of ammonia. Alkalies are an exception to this rule, as they render the nitrosulphates more stable, while they make the peroxide of hydrogen prone to decomposition; but the cases are different, the latter substance having none of the properties of an acid.

The basic character of alkalies, defined as their power of uniting with more oxygen, or with an acid playing the part of an oxygenous element, is illustrated by several curious decompositions. Thus, though grape-sugar reduces sulphate of copper with ease, cane-sugar alone does not readily do so, but when mixed with potash and boiled with the salt, suboxide of copper is produced, as in the mode of preparation of that oxide suggested by Boettger†, or the reduction of chloride of silver as proposed by Levol‡. Here the disposition of the organic matter to unite with oxygen is able to gratify itself when aided by the accessory affinity of the pot-

* *Ann. de Ch. et de Ph.* lx. 151.

† *Ann. der Pharm. und Chemie*, xxxix. 176.

‡ Berzelius, *Jahres Bericht*, bd. xxv.

ash for oxygen. That the potash in this state acts by aiding the oxidation, is seen by heating $Cu_2O$ with a solution of caustic potash, exposed to the air, when it oxidizes much more rapidly than when boiled with water alone*. When suboxide of copper is dissolved in ammonia it oxidizes with surprising rapidity. In this instance the hydrogen of the ammonia adds to its disposition as an alkali to absorb oxygen. The quick oxidation is not merely due to the fact of the suboxide being in a state of solution, because the soluble salts of the suboxide do not oxidize with such extraordinary ease, nor is it to be expected that they should, if we admit that the acid itself plays the part of oxygen. The accessory affinity of alkalies for oxygen is exhibited in many other cases of chemical action. Thus, colouring matters, such as deoxidized logwood, Brazil-wood, peach-wood, japan, fustic and catechu are oxidized more rapidly in contact with alkalies than in water alone; and various dyeing principles, such as orcin and erythrin, absorb oxygen with great avidity in the presence of ammonia. Sugar may be boiled with potash without decomposition, but when air is admitted, formic, melassic, and glucic acids are produced. Hydruret of benzule when exposed to air gradually absorbs oxygen and passes into benzoic acid, but in contact with potash this absorption is very much accelerated. The rapid decomposition of the gallates and of hematin in the presence of free alkali and air is a phænomenon of the same kind. In fact, numberless instances of this catalytic action of the alkalies are known to chemists.

We find the influence of an accessory oxidation in many cases of chemical union. Thus Campbell has shown † that the transformation of cyanide of potassium into cyanate of potash is much accelerated by the presence of the iron in yellow prussiate of potash, the iron being converted into oxide during the transformation. Here the iron plays the part of the protoxide of manganese in the cases of oxidation already referred to, or it perhaps bears a more direct relation to the action of lead in communicating a tendency to the base metals

* This experiment may be simply made as follows:—Three shallow evaporating basins of the same size and form, each containing the same quantity of suboxide of copper, are taken, and to one is added a solution of potash or soda; to the second, a solution of chloride of manganese; to the third, common water, taking care that the same volume of each fluid is added. The whole are now placed on a sand-bath, so as to be exposed to equal temperatures, and stirred occasionally. The suboxide of copper in the basin containing chloride of manganese oxidizes very rapidly; that in contact with the potash more slowly; and that with simple water is scarcely effected when both the others have lost their red colour. These actions are strictly in accordance with theory.

† Memoirs of Chemical Society, vol. i. p. 38.

to seize oxygen during the process of cupellation. The influence exerted by peroxide of manganese in first converting cyanide of potassium into cyanate of potash and afterwards into the carbonate of that base, is another instance of accessory affinity; for only a portion of the oxygen is derived from the oxide employed. The solution of an alloy of silver and platinum in nitric acid may be supposed to be a similar affinity. It is not necessary to believe that this is a case proving the communication of intestine motion to the atoms of platinum, by which it acquires the power of decomposing nitric acid *; for an equally simple explanation is given by assuming that the united affinities of platinum and silver are able to decompose nitric acid, both these affinities acting in one direction at the same time, and enabling the platinum to dissolve. We have only to suppose that the atoms of nitric acid are placed by the silver in a state of such tension that the platinum can now seize oxygen, which it could not do from the nitric acid when in a less tense state. The quartation of gold is obviously a phænomenon of the same kind. In these instances the interposing silver much reduces the cohesive or aggregative force of the platinum or gold, which opposes so strongly the action of nitric acid upon them. But when we have every atom of platinum or of gold separated by one of silver, great facility is given to the nitric acid to act upon these metals, especially when the silver at the same time aids them by its assistant affinity.

We have seen, in the consideration of the previous instances of catalysis, that the play of affinities was occasionally so nearly balanced, that a second disturbing cause determined the direction of the action. In the case of non-accendible phosphuretted hydrogen, the addition of another oxidizable body, $NO_4$, decided the union of oxygen with the gas. In accendible phosphuretted hydrogen the compound $PH_2$ played the same part. When the accessory agent is present in small quantity, the preponderating affinity of the body acted upon shows itself in the result. But, as the action is due to two affinities nearly equal in amount, it is easy to conceive that the increased quantity of the accessory agent may exactly balance affinities, and that the catalytic phænomenon will be prevented. Thus one-twentieth of the volume of binoxide of nitrogen, according to Graham †, added to accendible phosphuretted hydrogen, does not deprive it of inflammability, the bubbles of gas escaping into the air with a kind of explosion, although one-tenth volume of the same gas altogether prevents the accendibility. This nitric oxide,

* Liebig's Elements of Agriculture, 4th edit., p. 280.

† Phil. Mag., Third Series, vol. v. p. 405.

when pure, does not, like protoxide of nitrogen, render phosphuretted hydrogen spontaneously inflammable, the reason obviously being that its own affinity for oxygen is more powerful than that of the phosphuretted hydrogen. When added however in such small proportion to the accendible gas that the foreign constituent in it preponderates, then it becomes an accessory to the oxidation, though an increase of the quantity renders it more powerful, and prevents accendibility by itself seizing oxygen. Thus also larger volumes of gas, having an affinity for oxygen, but incapable like $NO_4$ of gratifying that desire under ordinary circumstances, may exactly balance the feeble affinity of the foreign accessory body and prevent oxidation. Five volumes of hydrogen, 2 volumes of carbonic acid, 1 volume of olefiant gas, and 1 volume sulphuretted hydrogen, deprive 1 volume of phosphuretted hydrogen of its spontaneous inflammability*. The very conception of a catalytic agent, on the view adopted, implies the exertion of an affinity, which is passed over or added to that of the body acted upon. If, therefore, a third body claim this added affinity, the increase of power being divided, may be insufficient to exert the force which it did when wholly applied to aid the affinity of one body. It may be this balancing of affinities which prevents the action of platinum on a mixture of oxygen and hydrogen. The platinum by its *surface affinity* condenses oxygen, and presenting it to hydrogen in a condensed form produces union. But in the presence of small quantities of certain oxidizable gases, such as sulphuretted hydrogen, carbonic oxide, and olefiant gases †, it ceases to exert this action, the assumption in this case being that the affinity of the added gases for oxygen balances that of hydrogen for the same gas.

This balancing of affinities may account for several phænomena otherwise inexplicable. On the decay of vegetable mould we find the hydrogen constantly diminishing in quantity until a certain period of decomposition, when the affinity of the carbon of the humus for its hydrogen balances the affinity of the surrounding oxygen. It seems to be the same balancing of affinities which renders corrosive sublimate so antiseptic in its properties; but, in this case, the balance results from the affinity of the second atom of chlorine in the bichloride of mercury for the hydrogen of the organic substance, thus preventing its union with oxygen. It is probable

* The influence which the vapours of turpentine exert in preventing the oxidation of phosphorus in the air is probably another instance of this balancing of affinities.

† Faraday, Phil. Mag., Third Series, vol. v. p. 105; Turner, Jameson's Journal, xi. 99 and 311.

that the same affinity of chlorine for hydrogen causes turpentine and the volatile oils to act catalytically in exploding chloride of nitrogen. The chlorine attracted by the hydrogen of these substances is drawn without the sphere of its attraction for nitrogen, and a disruption of the elements consequently ensues, compounds such as this resting on the very verge of separation between physical and chemical attraction. The antiseptic action of corrosive sublimate is very different from that exerted by sulphurous acid and sulphate of iron, these bodies acting by their superior affinity for oxygen, and neutralizing the power of the ferments or accessory oxidizers present in the organic body.

There is no difficulty in applying these notions of catalysis to organic compounds, which from the complexity of their molecules are peculiarly liable to change. If it once be admitted that an assisting affinity may exist in the sense defined in the present paper, then we see the same cause operating upon organic as well as inorganic molecules. When nitric acid acts on oxalic acid or starch, an inorganic body (a protosalt of manganese) lowers the temperature necessary for the oxidation, and exerts its influence until all the starch is converted into carbonic acid, being equally efficacious on the addition of more nitric acid and starch. Here the body acting as an assistant remains unchanged, and therefore continues its action *ad infinitum*, rendering it impossible to prepare oxalic acid from nitric acid and starch or sugar, carbonic acid being the only product*. Had the assistant oxidizer passed from solution during the progress of the oxidation, it could not of course continue its favourable effect, and a new portion of it must have been added. Here the inorganic salt enables the sugar to oxidize itself from the surrounding medium just as yeast does, the only difference being that the yeast itself suffers change, and therefore can only continue its action for a limited period. It is exactly in the same condition as a mixture of nitric acid and binoxide of nitrogen made to act on protochloride of tin. A small portion of the latter added to such a mixture is oxidized, but when the solution is heated until all the $NO_2$ is expelled, oxidation does not ensue on the addition of a new portion at the same low temperature as before. Now Saussure and Colin have shown that yeast only induces fermentation when it is in a position to absorb oxygen. It acts therefore strictly as binoxide of nitrogen, or a protosalt of manganese, in the previous

* In this it resembles the action of oxalic acid in converting an unlimited quantity of oxamide into oxalate of ammonia, with this difference, that the oxalic acid, which causes the change, may not be the same, but a regenerated portion, while the salt of manganese always remains unchanged.

instances, by adding its affinity for oxygen to that of the sugar, the added affinities of both completing the union. The only difference between these two decompositions is, that in one case the oxidizing agent is nitric acid, in the other it is water. The composition of sugar shows it to contain the elements of alcohol and carbonic acid *minus* an atom of water. In such a compound we have the affinity of carbon for hydrogen and of carbon for oxygen. The yeast by its nitrogen also exerts an affinity for hydrogen, and by its carbon for oxygen. The united affinities of the sugar and of the yeast acting upon water decompose it, its elements on their liberation being shared by the carbon of the sugar, for which it may be supposed to have the strongest affinities, $C_{12}\,H_{11}\,O_{11} + HO = 4CO_2 + 2\,(C_4\,H_6\,O_2)$. To show the exact similarity of the two processes of oxidation when the assisting body is either organic or inorganic, I may cite the curious manufacturing process for oxidizing oils in the method of dyeing Turkey-red used in this country, and included in Mercer's patent for that colour. It consists in oxidizing oils by blowing hot air through them, the oils being in contact with a solution of a salt of copper or of bran; the contact of either of these solutions is found very materially to accelerate the oxidation. The catalytic action of oxide of copper in evolving oxygen from hypochlorite of lime was adduced as showing its affinity for more oxygen, and this feeble affinity is well known and used empirically by all calico-printers, who are in the constant habit of mixing a salt of copper with their colours for the purpose of *ageing* them more speedily; in other words, of causing them to unite with oxygen. This also is the assisting cause in Mercer's process for oxidizing oils; bran in solution answers the same purpose from its affinity for oxygen. The addition of common salt or muriate of ammonia favours the oxidation in all the cases referred to, the oxidation proceeding much more quickly in their presence. No sub-chloride is ever formed, the action being purely catalytic, and probably depending on the conversion of the salt of copper into a chloride, the chlorine of which may be supposed to exert a slight affinity for the hydrogen of the compound, thus withdrawing it somewhat from the sphere of its own special attractions in the body; the copper now aiding the chlorine, delivers the hydrogen more easily into the power of the oxygen of the atmosphere. It is therefore immaterial whether the body exercising the assistant affinity be organic or inorganic, if the conditions be favourable to the exercise of this influence. The action of a body in acetous fermentation on the transformation of brandy into vinegar must be recognised

as a phænomenon of a like kind. We know that brandy may trickle without change over a large surface of wood shavings, through which air circulates at the heat of the human body, but that it is quickly converted into vinegar if brandy in the act of oxidation be mixed with it. Here the added ferment exerts its assisting affinity in precisely the same way as the salt of copper, when it aids the oxidation of oils or colours, or as protonitrate of manganese or peroxide of nitrogen during the oxidation of starch. The conversion of hydrogen and oxygen into water by the action of fermenting silk, cotton, or woody fibre, as observed by Saussure, is obviously a phænomenon of the same kind, and can only be exerted slowly and in the immediate vicinity of the assisting oxidizers, just as a ball of spongy platinum silently effects the union of these two gases.

In these cases we must admit that the action is independent of a state of intestine motion of the atoms of one compound molecule imparted to those of another, or, if we do not allow this, we must create two new powers and separate decompositions caused by inorganic bodies from those produced by organic compounds, although all the phænomena of the decomposition show them to belong to one category.

In a body in a state of such incessant change as the blood of living animals, it would naturally be expected that an added agency, such as that described, would render it prone to abnormal actions and oxidations, and in fact we do recognise by all the recent progress in the study of public hygeine that the addition of any oxidizing miasm or putrid matter to the blood does produce those changes which are known by their results in the different forms of disease. These and other catalytic agents no doubt exercise most important influence on the processes of animal life and on the action of medicaments on the system, but it would be foreign to the object of this paper to examine them in detail.

The limits of a paper such as this compel me to avoid including many other instances of catalytic decompositions which come under this explanation, or of drawing special attention to those which cannot be included in the present state of our knowledge. Thus diastase, acting on starch, converts it into sugar, but we have so little knowledge of the composition or properties of the first body, that it would be unwarrantable to embrace a case such as this. But in analogous changes produced by bodies which are understood, the same power is recognised. Sulphuric acid in converting starch into grape-sugar offers an example of combination which may fairly be examined by the same

method employed in investigating other decompositions. Graham has shown* that heat is evolved even on the addition of the 48th atomic proportion of water to sulphuric acid, or, in other words, that the affinity of that acid for water is not gratified as long as our instruments of research can follow the change. This is merely another proof of the doctrine with which I started, that there is no evidence of such a complete gratification of affinity as ever to merge entirely the attractions of the elements of any body. In the case referred to, the development of heat on each successive addition proves that the water is condensed on entering into union with the acid. When the heat of the sulphuric acid is artificially increased, this compound is broken up, for distillation drives off the water and concentrates the acid. Now when starch is in the presence of this weak combination of sulphuric acid and water, at a temperature at which the latter is just able to exert its affinity and again have it destroyed by heat, it is not at all extravagant to suppose that the starch may seize the water in its nascent state at the moment of expulsion, or even that it may be able to unite with the last atoms of the series of acid and water when presented in that condensed state, although it cannot do so when the water is free and not nascent. Any such union would explain the transformation of starch into grape-sugar, the change merely being in the acquisition of water, $C_{12} H_{10} O_{10} + 4HO = C_{12} H_{14} O_{14}$. The action here is not the same, but the very reverse of that which ensues in the preparation of æther. In the one case the sulphuric acid abstracts water, in the other it is the means of adding it, and the difference of the action depends on the relative strength of the acids employed. Without at all giving an opinion in favour of the necessity for the formation of sulphovinic acid, as supposed by Liebig †, or as to its not being an essential condition, as argued by Mitscherlich ‡, the final result is simply of the order now under consideration. In this decomposition the sulphuric or phosphoric acid is so strong that it combines with the water instead of yielding it, and the elevation of temperature essential to the change may either be due to the formation and after decomposition of sulphovinic acid, or it may be simply owing to the necessity of rendering the molecule of alcohol tense by heat, the elasticity of the æther and water both tending to break up the hydrate, the decomposition of which is determined by the presence of the strong acid now also aiding and abstracting the water. The final result is certainly

* Memoirs of Chemical Society, vol. i. p. 110.
† Geiger's *Pharmacie*, Band ii. S. 711 *et seq.*
‡ *Lehrbuch der Chemie*, Band i. S. 247 *et seq.*

purely catalytic in whatever light it is considered, although there may be more than one step in the process.

In conclusion, facts have been brought forward to show that there is at least as much probability in the view that the catalytic force is merely a modified form of chemical affinity exerted under peculiar conditions, as there is in ascribing it to an unknown power, or to the communication of an intestine motion to the atoms of a complex molecule. Numerous cases have been cited in which the action results when the assisting or catalytic body is not in a state of change, and attempts have been made to prove by new experiments that the catalytic body exercises its peculiar power *by acting in the same direction* as the body decomposing or entering into union, but under conditions in which its own affinity cannot always be gratified. The catalytic body is therefore a substance which acts by adding its own affinity to that of another body, or by exerting an attraction sufficient to effect decomposition under certain circumstances, without being powerful enough to overcome new conditions, such as elasticity and cohesion, which occasionally intervene and alter the expected result.

At the same time the theory is far from being fully proved; but if I have succeeded in rendering probable that the catalytic force is only chemical affinity recognised under an aspect which chemists have not been accustomed to view it, and exerted under conditions which can only be developed by close attention to details, it will not have been useless to direct increased study to this interesting class of phænomena.

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## CXCIV. *Analysis of the Ashes of the Orange-Tree* (Citrus aurantium). *By* Messrs. Thomas H. Rowney *and* Henry How.

FOR the materials used in the following analyses we are indebted to the kindness of Mr. Da Cumara, who had sent it over for investigation from his plantations on the island of St. Michel, being desirous to become acquainted with the mineral constituents of the orange-tree, which forms the principal wealth of his country. The analyses were performed under the direction of Dr. Hofmann in the laboratory of the Royal College of Chemistry.

To prepare the ashes in a fit state for analysis, the different parts of the plant were heated in an inclined, open Hessian crucible, until the carbon was consumed*. The ashes thus obtained were mixed with a small quantity of oxide of mer-

* To obtain the ash of the fruit, the oranges were cut into slices, and after separation of the seed dried on the sand-bath in a covered porcelain dish, and then burnt in a crucible.

cury and ignited a second time in a platinum capsule over a spirit-lamp, in order to reproduce the sulphates, which in the former process had been reduced to sulphides.

The same quantity of ash served to determine the potash and soda, sulphuric and phosphoric acids, perphosphate of iron, lime and magnesia, silicic acid and accidental sand and charcoal. For this purpose, the hydrochloric acid solution was evaporated to dryness, gently ignited and extracted with hydrochloric acid. The solution thus obtained was divided into different parts. The first portion served for the determination of the potash and soda.

For this purpose the acids, lime, magnesia, &c. were removed by baryta, the excess of baryta by carbonate of ammonia, and the ammoniacal salts by gentle ignition. The residue, potash and soda, were estimated partly by separating them by means of bichloride of platinum (analyses of the ashes of the root and seed) and partly by the indirect method, namely, by converting the mixed chlorides into sulphates, weighing these and ascertaining the amount of sulphuric acid by means of chloride of barium (analyses of the stem, leaves and fruit).

In the second portion, sulphuric and phosphoric acids were determined, the former as sulphate of baryta, the latter by neutralizing the filtrate from the former with ammonia and precipitating the phosphoric acid by means of sesquichloride of iron and acetate of potash. This precipitate was dissolved in hydrochloric acid, a sufficient quantity of tartaric acid was added, and the phosphoric acid estimated in the form of pyrophosphate of magnesia, by precipitating with ammonia, chloride of ammonium and sulphate of magnesia. The latter precipitate, frequently containing a small quantity of iron, was redissolved in hydrochloric acid, and after the addition of some tartaric acid reprecipitated by ammonia. A third portion served for the estimation of perphosphate of iron, lime and magnesia. For this purpose the liquid was neutralized with ammonia, some acetate of potash was added, and the solution strongly acidulated with acetic acid, in order to keep the phosphate of lime, which might be precipitated, in solution; on heating perphosphate of iron subsides, from which the sesquioxide of iron was calculated according to the formula $2Fe_2O_3+3PO_5$. From the filtrate the lime was precipitated by means of oxalate of ammonia, and after the separation of the lime, the magnesia by means of phosphate of soda. Chlorine and carbonic acid were determined in separate portions of the ash. In this manner the following experimental numbers were obtained:—

| | Roots. | | Stem. | | Leaves. | | Fruit. | | Seed. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | I. grms. | II. grms. | I. grms. | II. grms. | I. grms. | II. grms. | I. grms. | II. grms. | I. grms. | II. grms. |
| Quantity of ash employed for the general analysis ..... | 2·9360 | 3·07 | 3·5800<br>3·2350<br>4·6265 | 3·277 | 4·3040 | 4·653 | 3·7490 | 3·5415 | 1·3620 | 2·344 |
| Whole amount of the hydrochloric acid solution ..... | 164·634 | 154·059 | 229·956<br>222·683 | 139·376 | 202·696 | 171·503 | 207·520 | 169·273 | 171·100 | 181·45 |
| Hydrochloric acid solution for the alkalies ..... | 21·320 | 33·05 | 23·226 | 22·94 | 28·913 | 20·422 | 20·716 | 23·868 | 41·190 | 39·948 |
| Hydrochloric acid solution for sulphuric and phosphoric acids ..... | 24·989 | 35·442 | 39·393<br>27·456 | 25·99<br>16·18 | 23·616 | 22·574 | 33·013 | 18·22 | 25·630 | 34·288 |
| Hydrochloric acid solution for lime, magnesia, &c. ... | 31·959<br>25·686 | 39·155 | 38·506<br>36·693 | 26·331<br>25·827 | 22·830<br>21·550 | 24·324 | 27·356<br>21·716 | 22·568 | 23·945 | 27·391 |
| Quantity of ash employed for the estimation of chlorine | 1·4955 | 1·2235 | 1·1060 | 1·291 | 2·1230 | 1·927 | 1·9825 | 1·4595 | ·8270 | 0·6255 |
| Quantity of ash employed for the estimation of carbonic acid ..... | ·8400 | ..... | 0·884 | ..... | 1·5330 | 1·619 | 1·7660 | 1·5275 | 0·585 | |
| Quantity of the plant dried at 100° C. for the estimation of the amount of ash | 1·7175 | ..... | 1·1280 | ..... | 1·9892 | ..... | 3·5450 | ..... | 3·7825 | |

| | Roots. | | Stem. | | Leaves. | | Fruit. | | Seed. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | I. grms. | II. grms. | I. grms. | II. grms. | I. grms. | II. grms. | I. grms. | II. grms. | I. grms. | II. grms. |
| Silicic acid | ·0405 | 0·0445 | ·0330 | 0·04375 | ·1580 | 0·176 | ·0115 | 0·0135 | ·0140 | 0·0225 |
| Sand and charcoal | ·0125 | 0·0195 | ·0120 | 0·007 | ·0105 | 0·010 | ·0635 | 0·0575 | ·0785 | 0·1325 |
| Mixed chlorides of potassium and sodium | ·8185 | 0·846 | ..... | ..... | ..... | ..... | ..... | ..... | ·7913 | |
| Potassio-chloride of platinum | 1·9089 | ..... | ..... | ..... | ..... | ..... | ..... | ..... | 2·4861 | 4·294 |
| Chloride of sodium | ·2355 | 0·242 | ..... | ..... | ..... | ..... | ..... | ..... | ·0321 | 0·052 |
| Mixed sulphates of the alkalies | ..... | ..... | ·7772 | 0·784 | 1·4091 | 1·511 | 2·8349 | 2·7127 | | |
| Sulphuric acid contained in the sulphates of the alkalies | ..... | ..... | ·3772 | 0·379 | ·6863 | 0·739 | 1·3914 | 1·333 | | |
| Sulphate of baryta for sulphuric acid | ·3946 | 0·42 | ·3677 | 0·362 | ·4205 | 0·471 | ·3143 | 0·3028 | ·1769 | 0·306 |
| Pyrophosphate of magnesia for phosphoric acid | ·5007 | 0·53 | ·7244 | 0·73 | ·1673 | 0·19 | ·5060 | 0·483 | ·4372 | 0·7546 |
| Perphosphate of iron | ·0566 | 0·588 | ·0358 | 0·0375 | ·0355 | 0·0493 | ·0303 | 0·03 | ·0214 | 0·0397 |
| Carbonate of lime | 2·1059 | 2·21 | 3·7565 | 2·69 | 3·3296 | 3·61 | 1·2858 | 1·191 | ·4037 | 0·697 |
| Pyrophosphate of magnesia for magnesia | ·4454 | 0·47 | ·6675 | 0·469 | ·5282 | 0·547 | ·6545 | 0·59 | ·2929 | 0·4809 |
| Chloride of silver | ·0370 | 0·0275 | ·0055 | 0·008 | ·2640 | 0·245 | ·1425 | 0·111 | ·0169 | 0·0105 |
| Carbonic acid | 0·1600 | ..... | 0·146 | ..... | ·3560 | 0·372 | ·3600 | ·3090 | 0·04 | |
| Amount of ash left on incineration | ·0770 | ..... | ·0310 | ..... | ·2732 | ..... | ·1400 | ..... | ·1250 | |

These numbers correspond to the following per-centage:—

*Analysis of the Ashes of the Root. Composition directly found.*

Amount of ashes left by 100 parts of the root . . 4·48.

| | I. | II. | Mean. |
|---|---|---|---|
| Potash . . . . | 12·54 | 12·40 | 12·47 |
| Soda . . . . . | 3·72 | 3·57 | 3·64 |
| Lime . . . . . | 40·16 | 40·31 | 40·23 |
| Magnesia . . . | 5·55 | 5·60 | 5·57 |
| Sesquioxide of iron | 0·83 | 0·82 | 0·83 |
| Chloride of sodium | 1·01 | 0·91 | 0·95 |
| Phosphoric acid . | 10·80 | 10·93 | 10·86 |
| Sulphuric acid . . | 4·61 | 4·76 | 4·68 |
| Silicic acid . . . | 1·38 | 1·45 | 1·42 |
| Carbonic acid . . | 19·04 | 19·04 | 19·04 |
| Sand and charcoal | 0·42 | 0·63 | 0·53 |
| | 100·06 | 100·37 | 100·22 |

Per-centage of the ash after deduction of the unessential constituents, carbonic acid, sand and charcoal:—

| | |
|---|---|
| Potash . . . . | 15·43 |
| Soda . . . . . | 4·52 |
| Lime . . . . . | 49·89 |
| Magnesia. . . . | 6·91 |
| Sesquioxide of iron | 1·02 |
| Chloride of sodium | 1·18 |
| Phosphoric acid . | 13·47 |
| Sulphuric acid . . | 5·78 |
| Silicic acid . . . | 1·75 |
| | 100·00 |

*Analysis of the Ashes of the Stem.*

Amount of ashes left by 100 parts of the stem . . 2·74.

| | I. | II. | Mean. |
|---|---|---|---|
| Potash . . . . | 9·66 | 9·73 | 9·69 |
| Soda . . . . . | 2·61 | 2·47 | 2·54 |
| Lime . . . . . | 45·46 | 45·96 | 45·71 |
| Magnesia . . . | 5·28 | 5·24 | 5·26 |
| Sesquioxide of iron | 0·48 | 0·48 | 0·48 |
| Chloride of sodium | 0·19 | 0·24 | 0·21 |
| Phosphoric acid . | 14·18 | 14·17 | 14·17 |
| Sulphuric acid . . | 3·90 | 3·79 | 3·84 |
| Silicic acid . . . | 0·92 | 1·14 | 1·03 |
| Carbonic acid . . | 16·51 | 16·50 | 16·50 |
| Sand and charcoal | 0·33 | 0·21 | 0·27 |
| | 99·52 | 99·93 | 99·70 |

| | |
|---|---|
| Potash . . . . | 11·69 |
| Soda . . . . | 3·07 |
| Lime . . . . . | 55·13 |
| Magnesia . . . . | 6·34 |
| Sesquioxide of iron | 0·57 |
| Chloride of sodium | 0·25 |
| Phosphoric acid . | 17·09 |
| Sulphuric acid . . | 4·64 |
| Silicic acid . . . | 1·22 |
| | 100·00 |

*Analysis of the Ashes of the Leaves.*

Amount of ashes left by 100 parts of the leaves . . 13·73

| | I. | II. | Mean. |
|---|---|---|---|
| Potash . . . . | 12·87 | 12·48 | 12·67 |
| Soda . . . . . | 1·22 | 1·38 | 1·30 |
| Lime . . . . . | 43·32 | 43·44 | 43·38 |
| Magnesia . . . | 4·49 | 4·30 | 4·39 |
| Sesquioxide of iron | 0·36 | 0·44 | 0·40 |
| Chloride of sodium | 5·08 | 5·17 | 5·12 |
| Phosphoric acid . | 2·46 | 2·58 | 2·52 |
| Sulphuric acid . . | 3·35 | 3·47 | 3·41 |
| Silicic acid . . . | 3·67 | 3·78 | 3·72 |
| Carbonic acid . . | 23·22 | 22·97 | 23·09 |
| Sand and charcoal | 0·24 | 0·21 | 0·23 |
| | 100·28 | 100·22 | 100·23 |

| | |
|---|---|
| Potash . . . . | 16·51 |
| Soda . . . . . | 1·68 |
| Lime . . . . . | 56·38 |
| Magnesia . . . . | 5·72 |
| Sesquioxide of iron | 0·52 |
| Chloride of sodium | 6·66 |
| Phosphoric acid . | 3·27 |
| Sulphuric acid . . | 4·43 |
| Silicic acid . . . | 4·83 |
| | 100·00 |

*Analysis of the Ashes of the Fruit.*

Amount of ashes left by 100 parts of the fruit . . 3·94

| | I. | II. | Mean. |
|---|---|---|---|
| Potash . . . . | 28·21 | 28·32 | 28·26 |
| Soda . . . . . | 8·73 | 8·99 | 8·86 |
| Lime . . . . . | 19·20 | 18·83 | 19·02 |
| Magnesia . . . | 6·39 | 6·14 | 6·26 |
| Sesquioxide of iron | 0·35 | 0·36 | 0·35 |
| Chloride of sodium | 2·93 | 3·09 | 3·02 |
| Phosphoric acid . | 8·55 | 8·64 | 8·59 |
| Sulphuric acid . . | 2·88 | 2·93 | 2·90 |
| Silicic acid . . . | 0·31 | 0·38 | 0·34 |
| Carbonic acid . . | 20·38 | 20·22 | 20·30 |
| Sand and charcoal | 1·69 | 1·62 | 1·65 |
| | 99·62 | 99·52 | 99·55 |

| | |
|---|---|
| Potash . . . . | 36·42 |
| Soda . . . . . | 11·42 |
| Lime . . . . . | 24·52 |
| Magnesia . . . . | 8·06 |
| Sesquioxide of iron | 0·46 |
| Chloride of sodium | 3·87 |
| Phosphoric acid . | 11·07 |
| Sulphuric acid . . | 3·74 |
| Silicic acid . . . | 0·44 |
| | 100·00 |

*Analysis of the Ashes of the Seed.*

Amount of ashes left by 100 parts of the seed . . 3·30

| | I. | II. | Mean. |
|---|---|---|---|
| Potash . . . . | 35·22 | 35·29 | 35·26 |
| Soda . . . . . | 0·77 | 0·84 | 0·81 |
| Lime . . . . . | 16·59 | 16·65 | 16·62 |
| Magnesia . . . | 7·87 | 7·51 | 7·69 |
| Sesquioxide of iron | 0·68 | 0·72 | 0·70 |
| Chloride of sodium | 0·77 | 0·67 | 0·72 |
| Phosphoric acid . | 20·33 | 20·39 | 20·36 |
| Sulphuric acid . . | 4·46 | 4·48 | 4·47 |
| Silicic acid . . . | 1·02 | 0·96 | 0·99 |
| Carbonic acid . . | 6·83 | 6·83 | 6·83 |
| Sand and charcoal | 5·76 | 5·78 | 5·77 |
| | 100·30 | 100·12 | 100·22 |

| | |
|---|---|
| Potash . . . . . | 40·28 |
| Soda . . . . . | 0·92 |
| Lime . . . . . | 18·97 |
| Magnesia . . . . | 8·74 |
| Sesquioxide of iron | 0·80 |
| Chloride of sodium | 0·82 |
| Phosphoric acid . | 23·24 |
| Sulphuric acid . . | 5·10 |
| Silicic acid . . . | 1·13 |
| | 100·00 |

The preceding analyses furnish a new confirmation of the fact first observed by De Saussure, namely, that the largest amount of mineral constituents is deposited in those parts of the plant in which the process of assimilation appears to be most active. While the ash left by the root, stem, fruit and seed did not exceed from 3 to 4 per cent., the leaves left not less than 13 per cent. of fixed residue on incineration.

Regarding the composition of the different ashes, the great amount of carbonic acid found in the ashes of the root, the stem, and the fruit is at once obvious; proving that not only the fruit, but also the roots and stem, contain a large quantity of organic acids.

From the composition of the ashes of the root, the stem, and the leaves, the orange-tree belongs decidedly to the lime plants. In these three ashes the joint amount of lime and magnesia exceeds the quantity of the rest of the mineral constituents. In the ashes of the fruit and seed, however, the alkalies are as prevalent as they have been found in analogous cases. The amount of phosphoric acid (23·24) in the ash of the seed is considerable, as might be expected, still it is inferior to the quantities (34·81 and 42·02) which Mr. Souchay found on analysing the seeds of the citron (*Citrus Medica*) and quince-trees (*Pyrus Cydonia*). Nevertheless the ash of the orange-seed is very analogous in composition to the ashes of the last-mentioned seeds, as may be easily seen on comparing their analysis *.

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April 19, 1847.—The President, Mr. Brande, in the Chair.

"An Attempt to refute the reasoning of Liebig in favour of the Salt Radical Theory, by Professor Hare," was presented by the Author.

M. Redmond, Esq. was elected a Member of the Society.

The following papers were read:

* Liebig's Annals, liv. p. 343.

## CXCV. *On the Decomposition of Valerianic Acid by the Voltaic Current.* *By* H. Kolbe, *Ph.D.*

THE very remarkable changes which a series of organic compounds undergoes by means of the voltaic current, have induced me to make that mode of decomposition the subject of a thorough investigation. As however the numerous difficulties which present themselves in researches of this nature, and the immense extent of the field which opens before us, do not admit of the results being communicated in a complete and connected form, I beg to lay before the Chemical Society a short preliminary notice of the changes which valerianic acid undergoes when exposed to the oxidizing action of the voltaic current, reserving a more complete description of the products obtained till the investigation shall have been brought to a close.

When the voltaic current, excited by six pairs of Bunsen's carbo-zinc battery, is permitted to act on a concentrated neutral solution of valerianate of potash in the cold, two plates of platinum forming the electrodes, a brisk evolution of gas takes place simultaneously from both; the gases evolved consist of hydrogen, carbonic acid and a new carbo-hydrogen, but contain no traces of oxygen gas as long as the solution of valerianate of potash does not become too much exhausted. At the same time a light oily liquid separates at the surface, having an agreeable æthereal odour, and the alkaline solution ultimately consists chiefly of carbonate and bicarbonate of potash, the latter of which generally separates during the operation in a crystalline form.

The neutral æthereal oil is a mixture of two compounds; the one containing oxygen, the other perfectly free from it. By the action of an alcoholic solution of potash the former is decomposed, and the latter can then, by means of water, be separated unchanged. In the pure state it exists in the form of a light colourless æthereal oil, possessing an agreeable aromatic smell. It is insoluble in water, but soluble in alcohol and æther; it boils at 108° C. without decomposition, and has the composition $C_8 H_9$. Oxygen and iodine are without action upon it, but chlorine, bromine, and fuming nitric acid form with it products of substitution.

The oil containing oxygen, which in the first instance was found mixed with this substance, I have not yet been able to obtain in a pure state; but several circumstances render it more than probable that it is formed by the union of valerianic acid with the oxide of the above carbo-hydrogen. An alcoholic solution of potash treated with it is found to con-

tain as a product of decomposition a considerable amount of valerianate of potash. But on account of the small quantity of material which has been at my disposal, I have not succeeded in separating the alcohol $C_8 H_{10} O_2$, which must have been formed at the same time.

The gaseous carbo-hydrogen, which is evolved with the hydrogen, is a substance analogous to olefiant gas; it is characterized by a peculiar æthereal smell, and has a specific gravity double that of olefiant gas. It unites with chlorine even in the dark, forming a heavy oily liquid, havnig a marked similarity to chlorelayl, and is generally composed of a mixture of several products of substitution. Its rational composition is expressed by the formula $C_8 H_8$. The changes which valerianic acid undergoes, in accordance with the foregoing experiments, are capable of a very simple explanation, if we consider that acid as a conjugated combination of the carburetted hydrogen, or the radical $C_8 H_9$ with oxalic acid, in a similar manner to the new view taken of the constitution of acetic acid. For whilst by the addition of one atom of oxygen oxalic acid becomes converted into carbonic acid, this radical is set free; but a portion of it unites with the excess of oxygen to form an oxide, and this enters into combination with a portion of undecomposed valerianic acid, giving rise to a new æther, $C_8 H_9 O + C_8 H_9 C_2 O_3$.

Another portion of the radical is probably decomposed at the moment of its formation, in consequence of the concomitant evolution of heat into hydrogen and the gaseous carbohydrogen $C_8 H_8$. This latter view is supported by the fact, that if the temperature of the solution of valerianate of potash exceeds a certain point during the decomposition, not a single drop more of the ætherial oil is produced.

The following formula will throw light on this decomposition:—

$$\left.\begin{matrix} KO + C_8 H_9 C_2 O_3 \\ O \end{matrix}\right\} = \left\{\begin{matrix} KO + 2CO_2 \\ C_8 H_9. \end{matrix}\right.$$

Both butyric and acetic acids are acted on in a similar manner to valerianic acid; the products of decomposition of acetic acid are all gaseous, and appear to contain oxide of methyl. Butyric acid gives in addition to the gaseous compounds a volatile oil composed of $C_6 H_7$.

The minute description of this product will form the subject of a future memoir.

The foregoing investigation has been carried out during the late session in the laboratory of Dr. Lyon Playfair, as whose assistant I have been engaged during that time; and I

cannot allow this opportunity to pass by without thanking him for the kindness and liberality which he has shown in placing his laboratory at my disposal, in leaving so much of my time on my own hands, and in rendering me every assistance in his power.

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## CXCVI. *An Account of Experiments with Galvanic Couples immersed in pure water and in oxygenated water.* By Mr. Richard Adie.

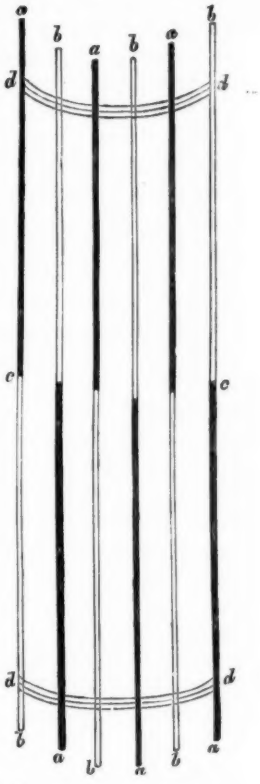
IN the years 1845 and 1846, I published in the Edinburgh Philosophical Journal two series of experiments, made with a view to prove that the action of the water battery was maintained by absorbing oxygen from the atmosphere. Some of these experiments* show that it is the oxygen only that is drawn from the atmosphere, and that the presence of the other component parts is unnecessary. But there was one given to show that zinc and copper elements placed in a hermetically sealed tube along with pure water did not act, there being no flocculent deposit of oxide of zinc, which is formed in abundance when a minute aperture admits the atmosphere to the contents of the tube. After a lapse of two years, I examined an arrangement of this kind which had been hermetically sealed since December 1844; there was no apparent change, the water was transparent, and the metals bright. I had scarcely put the tube down when it burst with violence; this fact immediately satisfied me that the water battery must have a true decomposition of water action when it acts on zinc associated with copper or any other metal less oxidizable than the copper, independent of the much more extensive effect due to atmospheric oxygen. It is from a desire to trace by experiment the double action of this battery that I respectfully submit for the consideration of the Society the following results:—

In fig. 1, *a a a* represents six pieces of zinc soldered at *c c* to a corresponding number of pieces of copper *b b b*, arranged alternately as in the figure, and insulated from one another by strands of thread, *d d d d*. These were placed inside a flint-glass test-tube, which was after their insertion drawn off at the blowpipe to a capillary point. The tube was now filled with pure water, and to dislodge the air from among the fibres of the thread, the water was repeatedly boiled, closing and re-opening the capillary point at each boiling. When the air was well-removed, the tube was hermetically sealed,

* Edinburgh New Phil. Journal, vol. xxxviii. p. 99, and vol. xl.

the water at the time of closing being near the boiling temperature. On cooling, the space left vacant by the contraction of the fluid was estimated to be $\frac{1}{70}$th of a cubic inch; the superficies of each plate $\frac{1}{4}$th of a superficial inch. From previous trials, I knew that when the above arrangement had a communication with the atmosphere, a flocculent deposit of the protoxide of zinc was soon perceived, which steadily increased. With the same hermetically sealed there was no such deposit; neither was there any perceptible change, until the bursting of the vessel after two years revealed another action of the battery. Judging from the thickness of the broken glass, I endeavoured at the time to make an approximate estimate of the volume of the gas generated, which in the vacant space of $\frac{1}{70}$th of a cubic inch, where it could lodge, produced pressure sufficient to burst the vessel: the result of my estimate gave less than a cubic inch of gas measured at the usual atmospheric pressure; for the development of which six zinc surfaces of $\frac{1}{4}$th of a superficial inch each had been two years in action. In a repetition of this experiment, with zinc filings in lieu of plates, a small quantity of gas was collected, and proved to be hydrogen.

Fig. 1.




Afterwards examining the inner surfaces of the fragments of the glass, the surface of the plates, and the fibres of the thread with a powerful lens, I found all of them covered with minute transparent crystals; the largest crop of these was on a copper surface opposite a spot on one of the zinc plates, to which nearly the whole of the corrosion of the metal appeared to have been confined. The red ground of the copper surface showed them most distinctly. On heating the copper the crystals parted with water of crystallization, and became circular white spots, very much resembling the protoxide of zinc.

My friend Mr. Waldie examined the thread; his process was, incinerating, dissolving the ash in hydrochloric acid, adding excess of potash, filtering to separate a trace of oxide

of iron, and treating the filtered liquid with hydrosulphuret of ammonia, which gave a yellowish white precipitate. This result proves that the minute transparent crystals among the fibres of the thread contained protoxide of zinc.

On a former occasion I employed either the air-pump or ebullition to deprive water used in exciting voltaic couples, of absorbed air. I gave preference to the method of boiling the water in the battery cell, as the more severe test, for showing how far a battery's action depended on oxygen from the atmosphere. The proof which appeared to me to furnish satisfactory evidence of the assistance given by absorbed oxygen, was when the indication in the galvanometer fell near to zero by prolonged boiling, and rose again when water holding dissolved air was thrown into the cell. According to this test, a zinc and platinum couple lose much of their action when excited by pure water boiled for near two hours. The galvanometer needles always indicated a slight action, however long the boiling was prolonged; but as I found when care was taken to have an atmosphere of steam resting on the surface of the boiling water the action of the couple was at its lowest, I was led to think that what remained might be due to oxygen from the atmosphere, which it was impossible to remove perfectly. The experiment given above renders this view no longer tenable; for if zinc and copper elements can at ordinary temperatures slowly generate gas, it must follow that all the elements less oxidizable than copper will at boiling temperatures possess, when associated with zinc, a voltaic action independent of oxygen from the atmosphere.

To try the effect of a zinc and copper couple excited by pure boiling water, I attached a pair of plates to a more sensitive galvanometer than I had hitherto used: the plates were placed in a Florence flask and covered to a depth of two inches with pure water previously distilled in glass vessels; there was only a small orifice in the cork at the top of the flask for a steam escape, in order to preserve the boiling surface from the atmosphere.

Previous to boiling, the galvanometer needle stood at 50°
Indication the moment boiling was about to begin . 70°
... after long boiling . . . . . 20°
A similar experiment with iron and copper elements:—
Indication previous to boiling . . . . . 20°
... at boiling . . . . . 46°
... after long boiling . . . . . 7°

In this experiment the indication rose on cooling to 30°, and afterwards fell back.

When silver or platinum was substituted for the copper the

results were in the same order, giving the highest action at the time the water is parting with dissolved air, and lowest when the water is thoroughly boiled. Where zinc is the positive element the action falls considerably, as the boiled water cools before it has time to re-absorb air. With a little common salt added to the water of a zinc and platinum couple, ebullition serves greatly to exalt the action, for the arrangement is no longer dependent on oxygen from the atmosphere.

These experiments, in extension of those I formerly submitted to the public through the Edinburgh Philosophical Journal, do not militate against the general conclusion then drawn, that the water battery supported its action by absorbing oxygen from the atmosphere; they only show that there is in addition a minute degree of action when two metallic elements are excited by pure water.

Perhaps the experiments of the most importance for determining the theory of the action of gas absorbing galvanic couples, are those where one metal only is excited by oxygenated water; to illustrate this action I made the following experiments:—

Two slips of zinc cut side by side from the same sheet were placed in a running brook, the one opposed to a rapid part of the current, the other in a still place at the edge. Connecting these in the usual manner with the galvanometer, there was a permanent deflection of 25°; and on changing the respective places of the plates in the stream without disturbing their attachments to the galvanometer, the needles immediately passed to the opposite side of the card; in both cases the piece of zinc in the current acted as a negative or platinode plate. With both plates in still water and a tube filled with oxygen inverted over one, the effect was the same. It is the greater supply of oxygen to the plate in the current which converts it into a negative or platinode. A cell containing two small silver wires and the cyanide of silver solution used for electro-plating was attached in place of the galvanometer, when, after a lapse of two hours, metallic silver was seen precipitated in a minute quantity on the silver wire connected with the piece of zinc in still water.

Two plates of iron were placed in the stream, under like conditions to the zinc; after two hours metallic silver was distinctly seen precipitated on the silver wire connected with the iron plate in still water.

The fact here shown, of two similar pieces of iron giving rise to a galvanic current capable of precipitating metallic silver, appears to me to be important, for it proves that the electricity in passing through the water intervening between

these two plates, either decomposes it with the aid of oxygen in solution, or that oxygenated water forms a binary compound, capable of acting as an electrolyte.

The fact of iron and oxygen uniting together at ordinary temperatures when moisture is present, is well known. It is the office performed by the water during this union, wherein lies the true ground of the theory of gas-absorbing batteries. A single plate of iron exposed to water and oxygen gas, has local differences on its surface which act in the same way as if the iron had been in two halves and placed in a stream in the manner described: the oxidation of the iron is developing a voltaic current which passes through the fluid from one point of the plate to another, either by a process of decomposition and re-composition of water, or by the decomposition of the compound formed by the solution of the gas in water.

The first of these views can only be supported by holding that the solution of oxygen so changes the affinities, that iron with its aid can at ordinary temperatures decompose water. I see no evidence sufficient to give probability to this hypothesis, while, if the second supposition be admitted to meet all the facts shown by experiment, it will establish the existence of an electrolyte more easily decomposed than water, and as universal in nature; and account for the very reduced action of zinc and copper elements excited by pure water freed from absorbed air or from oxygen gas, the active principle derived from the air.

I may here take occasion to add, that a saturated solution of carbonate of potash and soda in an open cylindrical vessel has so shut out the oxygen of the atmosphere from some pieces of iron immersed in it, that now, after two years and four months immersion, there is no rust on the surface of the iron.

The experiments with two similar pieces of zinc or of iron placed in a running stream, as already described, were performed during the cold weather of winter, with the temperature varying from 32° F. to 42°. On the return of a little warmer weather I recommenced the experiments with iron plates, from a wish to try if two similar pieces of iron could be made to develope a voltaic current of the same electromotive force as that derived from a platinum and iron couple excited by still water.

A piece of iron wire was cut into two equal lengths; each of those was bent into the form of a flat spiral (fig. 2), and a copper wire well-varnished was soldered to the iron at A, for connecting the plate with a small decomposing apparatus in the usual manner.

A pair of iron plates thus formed was taken to the banks of a small stream in Cheshire, called the Grange brook; one plate was placed in a current of moderate velocity, where the water poured through the interstices of the coils; the other plate was dropped into still water in a convenient place at the edge. In both plates the solderings at A projected above the surface and were kept dry.

Fig. 2.




When copper wire poles were placed in a decomposing cell filled with sulphate of copper solution, and connected with the galvanic couple formed of two pieces of iron (fig. 2), distinct evidence of the precipitation of metallic copper on the wire connected with the plate in still water, was observed after an hour's action, temperature 45°. One of the iron plates was now removed to a cell filled with water, and associated with a platinum plate, the arrangements for precipitating metallic copper remaining as before. With the temperature at 42°, the depositing of the metal did not proceed so actively as it had done with an iron plate in a current of water for a platinode.

When the decomposing cell was filled with a solution of sulphate of zinc, and zinc wire poles supplied, after three hours' action, temperature 46°, the wire in connexion with the iron plate in still water showed, with the aid of a lens, a distinct deposit of metallic zinc. Repeating this experiment with an iron and platinum couple in still water, the metallic deposit of zinc was again obtained, temperature 46°, the rate of action in both experiments being, as near as I could judge, the same.

The inference from these results is, that a piece of bright iron placed in a current of water performs the office of a piece of platinum, as well as the latter metal does when excited by still water.

The quantities of metal precipitated during two or three hours' action of these oxygen absorbing batteries is in no case sufficient to give results by weight. I have tried experiments of one week each, but the changes in the level of the stream and other sources of derangement, made me prefer trials of two or three hours each, where there is no difficulty in detecting any decided change in the rate of action.

The Grange brook is supplied with water almost wholly by the drainage of a rather poor clay soil, reposing on the new red sandstone formation of the district.

The plate in the centre of the stream shows less rusting than the one at the edge in still water; but judging from the analogous case of the copper sheathing of a ship, it should waste away the fastest, the particles of peroxide of iron as they are formed being removed by the force of the stream, while the voltaic current developed during this action only circulates to some other point of the same plate, or belongs to what is called local action.

From the above results, the benefit to be obtained in a constant battery by making the negative plate rotate, should be apparent; but to prevent waste it would still be necessary to employ one of the more costly metals, which are not liable to oxidation.

In concluding these experiments, I may again notice, that a tube of oxygen suspended over a plate of iron in still water has the same effect as the current of the stream, converting the oxygenated plate into a platinode. The carbonic acid present in all surface water may by some be thought to perform an essential part in the ordinary rusting of iron. But where every care is taken to exclude this gas from a tube filled with oxygen, a small quantity of water, and a piece of iron, the oxidation of the iron proceeds with rapidity, accompanied by changes which appear to me to preclude the idea that even a trace of carbonic acid can be essential. The oxygen gas disappears; at first an abundant formation of red or peroxide of iron is seen; then, after the supply of oxygen has decreased, the green-coloured protoxide is gradually formed. These two oxides afterwards begin slowly to unite, and form the well-known black or magnetic oxide. In an experiment of this kind every trace of the red and green-coloured oxides had disappeared at the end of three months from the time of closing the tube, and there remained only an inky precipitate, which was proved to be the black oxide of iron.

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## CXCVII. *Upon the Chemical Constitution of Metacetonic Acid, and some other Bodies related to it.* *By* E. Frankland, *Esq. and* H. Kolbe, *Ph.D.*

THE researches into the constitution of organic compounds certainly belong to the most interesting in chemistry. But they are always attended with more or less danger, and those who, leaving the safer road of experiment, plunge into the depths of hypothesis, and build up theories apparently ingenious, though often untenable, frequently stumble and fall amongst a host of contradictions. It is a common error,

as experience teaches, into which young chemists are very apt to fall, that, persuaded of the infallibility of their own views, and blind to well-founded objections, they endeavour to convince by quick and ready argument rather than by solid reasoning, and consequently they either offend others or feel themselves offended when contradicted.

When in the face of this danger we endeavour to advance views concerning the rational composition of some organic acids which do not accord with those generally received, we do it with a certain degree of timidity, and with the most strenuous endeavour to avoid those causes of error which have been pointed out. It is far from our intention to give a decided preference to the mode of viewing the subject here proposed, or indeed in any way to force our own opinion, nor is it unknown to us that even these views leave many facts unexplained; but we feel convinced that no detriment can accrue to the progress of science by looking at subjects of such importance with an impartial eye from all possible sides.

The starting-point of our experiments was the idea recently expressed by Berzelius, that acetic acid might be considered as a conjugate oxalic acid, as methyl oxalic acid, $C_2 H_3 C_2 O_3$. If this view of the subject, which explains so readily the conversion of acetic acid into chloracetic acid, and the remarkable reconversion of the latter into the former, and which has been further confirmed by the analogous relations of chlorocarbohyposulphuric acid and methyl-hyposulphuric acid, is correct, then the question arises whether it might not be extended to those other acids, so nearly related to acetic acid, namely, formic acid, metacetonic acid, butyric acid, benzoic acid, &c. We are of opinion that this question cannot *à priori* be answered in the negative; on the contrary, it appeared to us, after pursuing the subject further from that point of view, that the manifold metamorphoses which the above combinations undergo might be explained in a very simple manner, and we consequently have submitted the question to careful experimental examination; and we believe that we have gained a fact in support of the theory of conjugate compounds in its application to the acids in question, by the action which cyanide of ethyl exhibits with alkalies and acids.

When benzoic acid is supposed to consist of oxalic acid with the carburetted hydrogen, $C_{12} H_5$ (phenyle), as a conjunct, then it is evident that benzoe-nitrile obtained by Fehling* in distilling benzoate of ammonia, must be a cyanogen compound of the same carbo-hydrogen $= C_{12} H_5 Cy$. This mode of decomposition of phenyle-oxalic acid becomes thus

* Liebig's *Annalen*, xlix. p. 91.

completely analogous to the well-known formation of cyanogen by heating oxalate of ammonia, and to the formation of hydrocyanic acid from the formiate of ammonia.

Benzoe-nitrile, viewed as cyanide of phenyle, would then, together with the analogous body recently discovered by Schlieper*, valero-nitrile ($C_8 H_9 Cy$, cyanide of valyle), become allied to cyanide of ethyl; and as these bodies in contact with alkalies are so easily transformed into benzoic acid and valerianic acid, it is to be presumed that cyanide of ethyl under similar circumstances would become transformed into ammonia and metacetonic acid.

We prepared for this purpose pure cyanide of ethyl, according to the process of Pelouze, by the distillation of sulphovinate of potash with cyanide of potassium. The yellow-coloured liquid which passes over† was mixed with water, and separated again by chloride of sodium, dried over chloride of calcium, and lastly distilled in a bent tube freed from air and hermetically sealed. Purified in this manner cyanide of ethyl is a limpid colourless liquid, having an odour much resembling that of the terrible cacodyl. The analysis of the substance gave the following numbers:—

0·219 grm. gave 0·523 grm. of carbonic acid and 0·186 grm. of water.

| | | | Theory. |
|---|---|---|---|
| Carbon . . | 65·19 | 6 | 65·45 |
| Hydrogen . | 9·46 | 5 | 9·09 |
| Nitrogen . . | 25·35 | 1 | 25·46 |

To settle the question started above, this cyanide of ethyl was added drop by drop to a tolerably concentrated boiling solution of caustic potash, and the product of distillation returned to the retort as long as it retained any smell. During this operation a considerable portion of ammonia was given off. The alkaline residue distilled with sulphuric acid produced an acid liquid, which, neutralized with carbonate of silver, baryta, or lead, gave the corresponding salts of those bases. We had previously satisfied ourselves, by a carefully conducted experiment, that no formic acid was present in the acid solution.

The silver salt crystallizes from its aqueous solution in small acicular prisms. It is sparingly soluble in water, and the solution becomes blackened on boiling. The crystals dried over sulphuric acid *in vacuo* had the composition of metacetonate of silver.

* *Annalen der Chemie*, lix. p. 15.

† We found, in contradiction to Pelouze's statement, that cyanide of ethyl is tolerably soluble in water; but when the solution is saturated with common salt, it again separates unchanged and comes to the surface.

I. 0·211 grm. gave, when burnt with oxide of copper, 0·153 grm. carbonic acid and 0·055 grm. water.

II. 0·167 grm. gave on careful ignition 0·100 grm. of metallic silver.

| | | | |
|---|---|---|---|
| Carbon . . . | 19·77 | 6 | 19·90 |
| Hydrogen . . | 2·89 | 5 | 2·76 |
| Oxygen . . . | 13·06 | 3 | 13·27 |
| Oxide of silver . | 64·28 | 1 | 64·07 |
| | 100·00 | 15 | 100·00 |

The salt of barytes is very soluble in water; the solution of the salt evaporated to dryness and dried for a long time at 212°, gave the following numbers:—

I. 0·339 grm. gave 0·311 grm. carbonic acid and 0·116 grm. water.

II. 0·258 grm. gave 0·211 grm. sulphate of baryta.

| | | | Theory. |
|---|---|---|---|
| Carbon . . . | 24·98 | 6 | 25·46 |
| Hydrogen . . | 3·79 | 5 | 3·53 |
| Oxygen . . . | 17·58 | 3 | 16·99 |
| Barytes . . . | 53·65 | 1 | 54·02 |
| | 100·00 | | 100·00 |

The lead compound has the sweet taste of acetate of lead: it does not appear to crystallize, but dries up to a tough amorphous saline mass. A portion dried at 212° and *in vacuo* gave exactly the quantity of oxide of lead, corresponding to the formula PbO, $C_6 H_5 O_3$, namely,—

0·446 grm. gave 0·282 grm. oxide of lead and 0·021 grm. metallic lead, equivalent to 63·40 per cent. instead of 63·19.

From the above analyses, there can be no doubt that the acid product of the action of caustic potash upon cyanide of ethyl is metacetonic acid. The same result is produced by weak sulphuric acid (1 part acid to 2 parts water). The silver salt prepared from the acid product of distillation in this case exhibited the properties described above, and an estimation of the oxide of silver gave the following result:—

I. 0·150 grm. when ignited gave 0·090 grm. metallic silver, corresponding to 64·30 per cent. oxide of silver; the theoretical proportion being 64·07 per cent.

The mode of decomposition of cyanide of ethyl described is therefore quite analogous to that of benzoe-nitrile and valero-nitrile; and if metacetonic acid is considered as ethyl oxalic acid, with the formula $C_4 H_5 C_2 O_3$, the decomposition may be expressed by the equation

$$\left.\begin{matrix} C_4 H_5 Cy \\ KaO \\ 3HO \end{matrix}\right\} = \left\{\begin{matrix} KaO, C_4 H_5, C_2 O_3 \\ NH_3. \end{matrix}\right.$$

The assumption will be rendered still more palpable, if, as there is little doubt, at a future period we are able again to produce cyanide of ethyl from metacetonate of ammonia.

If, on the contrary, metacetonic acid is considered as an oxide of the radical $C_6 H_5$, then it must be assumed, that during the process of oxidation the two atoms of carbon, in the cyanogen, amalgamate themselves, as it were, with ethyl, in order to form the new radical metacetyl. Setting aside the great improbability attached to such an assumption, to which there would be at present no analogous case, we feel justified in giving preference to the former explanation, because it is the more simple, and because it completely agrees with the known transformation of cyanogen and water into oxalic acid and ammonia; and if, as one of us has found, valerianic acid, placed in the circuit of the voltaic current, by the assumption of 1 atom of oxygen, becomes converted into carbonic acid and the carbo-hydrogen $C_8 H_9$, we consider that our view has gained by that fact an additional support, and that the acid in question contains that carbo-hydrogen in conjugate combination with oxalic acid.

The foregoing observations lead to a great simplification of our hypothesis in regard to organic radicals, inasmuch as they do away with the necessity of supposing a specific radical for each acid belonging to an alcohol. The series of radicals which are produced by the addition of one or more equivalents of the carbo-hydrogen $C_2 H_2$ to 1 equivalent of hydrogen, namely $C_2 H_3$, $C_4 H_5$, &c., the hydrated oxides of which form the alcohols, are again found in accordance with our view in the acids derived from them, conjoined with oxalic acid. It may be conceived that the oxygen, in converting alcohol or oxide of ethyl into acetic acid, first acts upon the equivalent of carbo-hydrogen $C_2 H_2$, which alone distinguishes ethyl from methyl, and that the successive products of oxidation of this body take up the remaining radical methyl into conjugate combination; thus in the formation of aldehyde and acetic acid,

$$\left.\begin{matrix} C_4 H_5 O \\ 2O \end{matrix}\right\} = \left\{\begin{matrix} C_2 H_3, C_2 HO_2 \\ HO \end{matrix}\right.$$

$$\left.\begin{matrix} C_4 H_5 O \\ 3O \end{matrix}\right\} = \left\{\begin{matrix} C_2 H_3, C_2 O_2 \\ 2HO \end{matrix}\right.$$

Moreover, it cannot be denied that our ideas concerning the functions performed by compound radicals are very much enlarged by these considerations. For when we find methyl and ethyl combining like the electro-positive inorganic elements with the electro-negative non-metallic substances, the

property which they also exhibit of uniting with oxalic acid, hyposulphuric acid, and with other, perhaps even neutral, bodies to form conjugate compounds, evinces such an extensive range of properties as is nowhere to be met with amongst the more narrowly defined powers of combination of inorganic substances; and it is probable that nature, when she brings forth the innumerable and manifold products of the organic kingdom by a wonderful combination of those few elements which are at her disposal, may likewise make use of these supposed extensive combining powers of the organic radicals, as the simplest means of accomplishing her greatest works.

We beg to express our warmest thanks to Dr. Lyon Playfair for the use of his laboratory and apparatus in carrying out the above investigation, and for the uniform kindness which we as his assistants have experienced at his hands.

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May 3, 1847.—Thomas Graham, Esq., Vice-President, in the Chair.

It was proposed by the Council, that Law 9 of the Society be altered and do stand thus: "The Ordinary Meetings of the Society shall be held on the first and third Mondays of every month, from November to June inclusive, except the month of January, when the Society shall meet on the third Monday of the month only."

The following communications were read:—

Additions to his paper "On Voltaic Couples." By R. Adie, Esq.

Note on the Measurements of the Double Sulphates of Zinc and Soda, and of Magnesia and Soda. By W. H. Miller, M.A., Professor of Mineralogy, Cambridge.

The crystals were not good enough for me to obtain a very satisfactory result from a few observations; they are however sufficiently good to show that they are isomorphous.

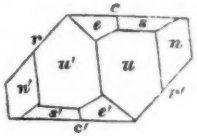
The crystals belong to the oblique prismatic system.

The angles between normals to the faces are—for the oxide of zinc salt,

$n\,n'$ 113° 4
$u\,u'$ 74° 12

the angle between a normal to $c$ and the intersection of

$u, u' = 10°\ 22'$
$u\,c$ 83° 46′
$r\,c$ 49° 54′




The symbols of the simple forms, in the notation which I use, are—

$c$ 001, $r$ $\bar{1}01$, $n$ 110,
$u$ 120, $e$ 011, $s$ 121.

The faces of the magnesian salt are more irregular than those of the former, so that I cannot pretend to determine the difference between the angles of these crystals.

The angles given above must be considered as rough approximations only. In a little time perhaps I may be able to obtain more accurate values of them.

## CXCVIII. *On the Analysis of Hop-Ash.* By Henry Watts, *B.A., Assistant in the Laboratory of University College, London.*

THE hops, the ash of which forms the subject of the following analysis, were of the variety called "the Grape." They were grown last year at Hawkhurst in Kent, on a good soil, being a stiff clay loam resting on the Hastings sand. The produce was 12 cwt. per acre, which is rather above the average produce of the district, the quantity being ascertained after the hops had been taken from the kiln, cooled and bagged.

The hops in this state lost $11\frac{1}{2}$ per cent. by drying at 212°.

1000 grs. of the hops in the same state burnt in an earthen crucible yielded in four experiments, 62, 65, 67 and 64 grs. of ash. The mean of these is 64·5; hence the quantity of ash is about $6\frac{1}{2}$ per cent.

The appearance of the ash was highly ferruginous.

### *Qualitative Analysis.*

A portion of the ash was exhausted with water, and the soluble and insoluble portions separately examined.

The soluble portion of the ash was found by the usual reagents to contain carbonic, sulphuric, phosphoric and silicic acids and chlorine. The bases were potash and a little soda.

The insoluble portion, in like manner, was found to contain lime, magnesia, alumina and peroxide of iron, in combination with carbonic and phosphoric acids, together with a considerable quantity of siliceous sandy matter insoluble in acids, and a little unburnt charcoal. This after ignition was further examined by fusion with carbonate of soda, and found to consist of silica, with traces of alumina, oxide of iron and lime. The presence of phosphate of alumina being unexpected, great pains were taken in this part of the analysis to place the matter beyond question.

### *Quantitative Analysis.*

#### A. *Proportions of soluble and insoluble matter.*

1. 100 grs. of the ash (recently ignited) were boiled in water. The insoluble portion was collected on a weighed filter and thoroughly washed.

Insoluble matter dried at 300° weighed 64·72 grs.
Therefore soluble matter ... 35·28 ...

2. 50 grs. of ash treated in the same manner gave—
Insoluble matter = 31·87 = 63·74 per cent.
Soluble matter = 18·13 = 36·26 ...

3. These results differ by about 1 per cent.; the difference probably arises from the slow decomposition of an alkaline silicate by continued digestion in hot water.

Taking the mean of the two results, we have—
Matter insoluble in water = 64·23 per cent.
... soluble ... = 35·77 ...

B. *Matter soluble in water.*

I. *Acids and Chlorine.*—1. Alkaline liquid from 100 grs. of ash (A. 1) concentrated by evaporation to the bulk of 1000 water grain-measures, then divided into four equal portions.

2. First portion decomposed by sulphuric acid in flask-apparatus gave 0·54 gr. of carbonic acid = 2·16 per cent.

3. Second portion treated with chloride of barium and nitric acid gave 6·03 grs. of sulphate of baryta: therefore 2·07 grs. of sulphuric acid = 8·28 per cent.

4. Third portion treated with nitrate of silver and nitric acid gave 2·29 grs. of chloride of silver: therefore 0·564 gr. of chlorine = 2·26 per cent.

5. Fourth portion mixed with solution of pernitrate of iron made by dissolving 3·68 grs. of good iron wire (harpsichord wire) in nitric acid, and therefore containing 5·26 grs. of peroxide of iron. The liquid being then treated with excess of ammonia, the precipitate washed, dried and ignited, was found to weigh 5·47 grs.; and deducting 5·26 grs. of peroxide of iron, there remains 0·21 gr. of phosphoric acid, or 0·84 per cent.

II. *Silica and Alkalies.*—1. Alkaline liquid from 50 grs. of ash (A. 2) acidulated with hydrochloric acid and evaporated to dryness; residue digested in dilute hydrochloric acid, silica collected on filter, washed, dried and ignited, weighed 1·22 gr. = 2·44 per cent.

2. Filtered solution treated with baryta-water to separate sulphuric and phosphoric acids; excess of baryta removed by carbonate of ammonia; filtered liquid evaporated to dryness, and ammoniacal salts driven off by ignition; the residue consisting of chlorides of fixed alkalies, weighed 16 grs. = 32 per cent.

3. 2·25 grs. of these mixed chlorides dissolved in water and treated in the usual manner with $3\frac{3}{4}$ times their weight of sodio-chloride of platinum, gave 7·06 grs. of chloride of platinum and potassium, corresponding to 2·157 grs. of chloride of potassium. Now 2·25 : 32 : : 2·157 : 30·68; we have therefore

| | | | | |
|---|---|---|---|---|
| Chloride of potassium | 30·68 | p. c. = | 19·41 | p. c. of potash. |
| ... sodium | 1·32 | ... = | 0·70 | ... of soda. |
| | 32·00 | | 20·11 | |

C. *Matter insoluble in water.*

I. *Siliceous sandy matter.*—Insoluble matter from 100 grs. of ash (A. 1) boiled in hydrochloric acid; liquid evaporated to dryness to render silica perfectly insoluble; residue digested in dilute hydrochloric acid; undissolved matter, consisting of silica and charcoal, collected on weighed filter, washed and dried at 300°.

| | |
|---|---|
| Silica and charcoal weighed . | 18·26 grs. |
| Silica (after ignition) . . . | 15·44 ... |
| therefore Charcoal . . . . . | 2·82 ... |

II. *Earthy Phosphates.*—1. Filtered solution (C. I.) treated with excess of ammonia yielded a precipitate which being washed, dried and ignited, gave of earthy phosphates 27·26 grs.

2. Phosphates, after ignition, dissolved in hot hydrochloric acid and reprecipitated by ammonia; precipitate digested in warm acetic acid to dissolve phosphates of lime and magnesia; the insoluble portion consisting of phosphates of iron and alumina weighed 8·25 grs.

3. Phosphates of iron and alumina redissolved in hot hydrochloric acid; solution boiled with excess of caustic potash, undissolved portion collected on filter, washed, dried and ignited, gave

| | |
|---|---|
| Weight of phosphate of iron . | = 4·57 grs. |
| Therefore phosphate of alumina | = 3·68 ... |
| | 8·25 ... |

4. Alkaline solution (C. II. 3) boiled with sal-ammoniac, gave a precipitate of phosphate of alumina, which weighed only 1·8 gr. instead of 3·68; but the liquid filtered from this precipitate gave, when treated by Berthier's process, a quantity of phosphoric acid weighing 1·91 gr., which, added to 1·80 gr., gives 3·71 grs. for the quantity of phosphate of alumina, differing by only 0·03 gr. from 3·68 grs. We may infer from this that the quantity of phosphoric acid in combination with alumina is about 2·5 per cent.

5. To determine the quantity of phosphoric acid in combination with oxide of iron, the 4·57 grs. of phosphate of iron (C. II. 3) was redissolved in hot hydrochloric acid, and the solution treated with ammonia and sulphuret of ammonium:

the sulphuret of iron, after washing, was oxidized by nitric acid and the oxide of iron precipitated by ammonia. The result was

| | | |
|---|---|---|
| | Oxide of iron . . . . | 2·71 grs. |
| therefore | Phosphoric acid . . . | 1·86 ... |
| | | 4·57 ... |

6. Acetic acid solution (C. II. 2) containing the phosphates of lime and magnesia treated with oxalate of ammonia; oxalate of lime washed, dried and ignited, gave 14·23 grs. of carbonate of lime = 7·97 grs. of lime.

7. Liquid filtered from lime, treated with excess of ammonia, gave

Pyrophosphate of magnesia 4·37 = { 2·77 phosphoric acid. / 1·60 magnesia.

8. The quantity of phosphoric acid in combination with lime was determined by difference; thus

Total quantity of earthy phosphates = 27·26 grs.

| | | |
|---|---|---|
| Phosphates of iron and alumina | 8·25 grs. | |
| Phosphate of magnesia . . . | 4·37 ... | |
| Lime . . . . . | 7·97 ... | |
| Making together . . . . . | —— | 20·59 ... |
| Therefore phosphoric acid . . | | 6·67 ... |

This is very nearly the quantity required to form the tribasic phosphate; for the combining number of lime being 28, and that of phosphoric acid 71·38, we have

$$84 : 71{\cdot}38 :: 7{\cdot}97 : 6{\cdot}77,$$

which result differs by 0·1 from 6·67.

The quantity of phosphate of lime is $7{\cdot}97 + 6{\cdot}67 = 14{\cdot}64$.

9. If we reckon as above (C. II. 4) the quantity of phosphoric acid in the phosphate of alumina at 2·5 per cent., we have for the total quantity of phosphoric acid in the insoluble part of the ash $6{\cdot}67 + 2{\cdot}77 + 1{\cdot}86 + 2{\cdot}50 = 13{\cdot}80$. Adding to this the quantity contained in the soluble portion (B. I. 5), viz. 0·84, the total amount of phosphoric acid will be 14·64 per cent.

III. *Carbonates of Lime and Magnesia.*—1. Liquid filtered from precipitated phosphates (C. II. 1), boiled with oxalate of ammonia, precipitate washed, dried and ignited, gave carbonate of lime 11·04 grs., containing 6·18 grs. of lime and 4·86 grs. of carbonic acid.

2. Filtrate containing magnesia evaporated to dryness; residue ignited to drive off ammoniacal salts and redissolved in hydrochloric acid. Solution mixed with carbonate of soda

in excess, boiled briskly for half an hour and filtered; filtrate evaporated quickly to dryness, residue digested in boiling water, and undissolved portion added to precipitate on filter; precipitate of carbonate of magnesia washed, dried and ignited, gave 3·74 grs. of magnesia.

To determine the quantity of carbonic acid in combination with this, we have 20·67 : 22 :: 3·74 : 3·99, this added to 3·74 grs. of magnesia, gives 7·73 grs. of carbonate of magnesia.

3. From this it appears that the total quantity of carbonic acid in combination with lime and magnesia is 4·86 + 3·99 = 8·85 grs.

To verify this, the carbonic acid was determined directly from the insoluble portion of 50 grs. of ash (A. 2). This insoluble matter weighed 31·87 grs. or 63·74 per cent. Of this, 14·27 grs. decomposed by hydrochloric acid in flask apparatus, gave 2·07 grs. of carbonic acid. Now

14·27 : 63·74 :: 2·07 : 9·24.

This quantity differs by 0·39 from 8·85, the calculated quantity. The excess is probably due to the escape of a little hydrochloric acid during the boiling of the liquid in the flask apparatus. The estimation of the lime and magnesia is more to be depended upon than that of the carbonic acid.

*Summary.*

The phosphoric, carbonic and silicic acids exist both in the soluble and insoluble portions of the ash.

The total quantity of phosphoric acid has been already estimated approximately at 14·64 per cent. (C. II. 9).

The quantity of carbonic acid in the soluble portion is 2·16 (B. I. 2), and in the insoluble 8·85 (C. III. 3), making together 11·01 per cent.

The quantity of silica in the soluble part is 2·44 (B. II. 1), and in the insoluble part 15·44 (C. I.), making together 17·88 per cent.

The total quantity of lime is 14·15 per cent., viz. 7·97 in the phosphate, and 6·18 in the carbonate (C. II. 6, and C. III. 1).

The magnesia amounts to 5·34 per cent., 1·60 being in the state of phosphate (C. II. 7) and 3·74 in that of carbonate.

The total quantity of alkaline bases (potash and soda) is 20·11 per cent. (B. II. 3). From this we must deduct the quantity of oxygen corresponding to 2·26 of chlorine (B. I. 4), viz. 0·51, because portions of the potassium and sodium are in the state of chlorides.

Finally, then, we have for the constituents of the hop-ash,—

I. *Acids.*

| | | |
|---|---|---|
| Phosphoric acid . . . . | 14·64 | |
| Sulphuric acid . . . . . | 8·28 | |
| Silicic acid . . . . . | 17·88 | |
| Carbonic acid . . . . . | 11·01 | |
| Chlorine . . . . . | 2·26 | |
| | —— | 54·07 |

II. *Bases.*

| | | |
|---|---|---|
| Potash . . . . . | 19·41 | |
| Soda . . . . . | 0·70 | |
| Lime . . . . . | 14·15 | |
| Magnesia . . . . . | 5·34 | |
| Alumina . . . . . | 1·18 | |
| Peroxide of iron . . . . | 2·71 | |
| | 43·49 | |
| Deduct oxygen . | 0·51 | |
| | —— | 42·98 |
| Charcoal and loss . . . . . | | 2·95 |
| | | 100·00 |

These materials we may suppose to be arranged as follows:—

I. *Matter soluble in water.*

| | | |
|---|---|---|
| Chloride of sodium . . . | 1·32 | |
| Chloride of potassium . . | 3·09 | |
| Carbonate of potash . . . | 6·79 | |
| Sulphate of potash . . . | 18·05 | |
| Phosphate (tribasic) . . . | 2·50 | |
| Silicate of potash . . . | 3·83 | |
| | —— | 35·58 |

II. *Matter soluble in acids.*

| | | |
|---|---|---|
| Carbonate of lime . . . | 11·04 | |
| Carbonate of magnesia . . | 7·73 | |
| Phosphate of lime . . . | 14·64 | |
| Phosphate of magnesia . . | 4·37 | |
| Phosphate of alumina . . | 3·68 | |
| Phosphate of iron . . . . | 4·57 | |
| | —— | 46·03 |

III. *Insoluble matter.*

| | | |
|---|---|---|
| Silica, &c. . . . . | 15·44 | |
| Charcoal . . . . . | 2·82 | |
| | —— | 18·26 |
| | | 99·87 |

The sum of the soluble ingredients thus determined, viz.

35·58, differs by only 0·19 from 35·77, the amount of the same directly determined (A. 3).

The sum of the components which are insoluble in water, viz. 46·03 + 18·26 = 64·29, differs by 0·06 from the quantity of the same directly determined, viz. 64·23.

The loss on the whole analysis is 0·13 per cent.

*Quantities of materials removed from an acre of land by the crop.*

The produce, as stated at the commencement of the paper, was 12 cwt. per acre, and the amount of ash is 6½ per cent. This gives 87 lbs. 6 ozs. of ash to the produce of an acre. Hence it is easy to calculate the quantities of the several mineral ingredients of the hops removed from an acre. In this estimate no account need be taken of the bines, since they are rotted and returned as manure to the soil.

The quantities of the several constituents are as follows:—

| | lbs. | oz. |
|---|---|---|
| Phosphoric acid | 12 | 13 |
| Potash | 17 | 0 |
| Lime | 12 | 6 |
| Magnesia | 4 | 11 |
| Sulphuric acid | 7 | 4 |
| Silica | 15 | 10 |
| Alumina, oxide of iron and common salt | 6 | 15 |
| | 76 | 11 |

By way of comparison the following statement of the inorganic materials removed by a heavy crop of grain (not including straw or chaff) of the estimated yield of 42 bushels to an acre*, extracted from the excellent report of Messrs. Way and Ogston in the Agricultural Journal, vol. vii. part 2, may prove interesting.

From each acre were removed,—

| | lbs. | oz. |
|---|---|---|
| Phosphoric acid | 21 | 4 |
| Potash | 13 | 1 |
| Magnesia | 5 | 5 |
| Silica, sulphuric acid, oxide of iron, and soda | 3 | 7 |
| | 43 | 1 |

It is well-known that the cultivation of hops is carried on by a most lavish application of farm-yard manure to the ruin

* Specimen No. 41, p. 631.

of every other crop, the rest of the land being defrauded of its due share of nourishment to supply the increasing demands of the hop-garden: and further, that in this cultivation there is no relief by alternating crops or fallows, unless the occasional failures from blight and other causes may be so termed. The quantity of alkali thus removed every year exceeds that of a very heavy crop of grain, while the phosphoric acid amounts to more than half that of the latter. It is probable also that the quantities of phosphoric and sulphuric acids present in the ash do not indicate the total quantities of sulphur and phosphorus removed from the soil, inasmuch as portions of these elements may exist in the plants as proteine-compounds.

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May 17, 1847.—The President in the Chair.

Messrs. Way and Ogden presented a copy of their "Report on the Analysis of the Ashes of Plants."

Heinrich Kolbe, Ph.D. was elected a Foreign Member, and Mr. Alfred Allchin a Member of the Society.

Resolved: That the alterations proposed by the Council in Law 9 be adopted.

The following communications were read:—

Additions to his paper "On Catalytic Action." By Lyon Playfair, Ph.D.

Additions to his paper "On Crystallography, &c." By H. B. Leeson, M.D.*

"On a Method of Analysis for Bodies containing Nitric Acid, &c." By Walter Crum, Esq.

"On Creatin and Creatinin in Urine." By Prof. Liebig. (Translated and communicated by Dr. Hofmann.)

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June 7, 1847.—The President in the Chair.

The following papers were read:—

## CXCIX. *On the Hydrates of Nitric Acid.* *By* Mr. Arthur Smith, *Assistant in the Laboratory of University College, London.*

SOME doubt still hanging over the composition of the hydrates of nitric acid, especially of the first hydrate, I was induced to try some experiments with a view of diminishing this uncertainty. For this purpose a quantity of the red fuming acid was procured, which I examined before commencing my experiments very carefully for chlorine, and found to be perfectly free from that impurity, and to have a specific gravity of 1·500.

* The publication of this paper is unavoidably deferred to the end of the present volume.

Fourteen ounces of acid of the above-named strength were mixed with 7 ounces of commercial oil of vitriol, and distilled in a sand-bath over a gas flame; the first 2 ounces that came over were rejected, and the receiver changed directly; the red fumes of nitrous acid were observed to fill the interior of the retort. The acid collected was almost as dark in colour as the acid before distillation. Its specific gravity was 1·522, and it turned out to be perfectly free from the smallest trace of sulphuric acid.

I also examined the first two ounces of acid that came over very carefully for chlorine, and found it to contain scarcely a trace, nitrate of silver producing only a slight opalescence, and that which came over afterwards, being the portion that I selected for my experiments, contained none at all. This last acid, when diluted with water, gave off nitric oxide gas with a burst of effervescence, which was the principal reason why it could not be employed to ascertain the exact amount of real acid by saturation in its present dark-coloured condition.

The apparatus employed in decolorizing the nitric acid consisted of a capacious retort, capable of holding about a pint, to the beak of which was attached a large tubulated receiver, which was kept surrounded with water, to condense any little acid that might come over during the process; to the tubulure of this receiver was adapted a glass tube, bent at right angles, fitting tightly with a cork, the other extremity being in connexion with a large gas-holder, which was kept constantly filled with water, to be used as an aspirator. To the tubulure of the retort was also fitted a long glass tube bent at right angles, the one end of which terminated within an inch of its bottom, whilst the other was in connexion with a couple of tubes, each 2 feet 11 inches long, arranged side by side, and connected by means of a tube of a smaller diameter bent like the letter U.

These long tubes, through which the air was to be aspired, were filled, the one with dried chloride of calcium, and the other with pumice-stone moistened with oil of vitriol, and by these means the absence of all moisture from the air was ensured.

In decolorizing the acid a quantity amounting to 6 or 7 ounces was introduced into the retort, and after having ascertained that the whole apparatus was perfectly tight, heat was applied to the bottom of a small sand-bath in which the retort was immersed, and the temperature kept up carefully to 170° F. Then, by removing the plug at the bottom of the gas-holder, and turning the stop-cock at the top, which was in connexion with the apparatus, a constant flow of perfectly dry air was caused to bubble through the nitric acid in the

retort, the level of which was kept 2 or 3 inches above the orifice of the tube in the interior, the only passage for the air being through the long desiccating tubes. Aspiration kept up for two or three hours was found to be generally sufficient to decolorize completely 6 or 7 ounces of nitric acid.

The acid before decolorization had a specific gravity of 1·522, and after the process fell to 1·503. Fifty grs. of the colourless nitric acid were accurately weighed out in a stoppered specific gravity bottle, to which was cautiously added, whilst in the bottle, with a view to prevent any loss from splashing, a known weight of perfectly pure carbonate of soda, recently ignited in a porcelain crucible, until the solution was perfectly neutral to test-paper. The absence of any sulphate or chloride in the carbonate had been previously ascertained.

I. Carbonate of soda required 40·23 grs.

II. Carbonate of soda required 40·23 grs.

The quantity of carbonate of soda that 50 grs. of acid required for saturation, then, was 40·23 grs., which corresponds to 40·78 grs. of nitric acid, or 81·56 per cent.

An acid containing $1\frac{1}{2}$ equiv. of water would contain in 100 parts—

| | |
|---|---|
| Real nitric acid . . . . | 80 |
| Water . . . . . | 20 |
| | 100 |

A portion of the prepared acid, amounting to about 5 ounces, was introduced into a small retort, through the tubulure of which was fitted tightly, by means of a stopping of moist clay, a delicate thermometer, which was kept immersed in the liquid. The acid began to boil at 190°, and before the distillation had come to an end it had risen to 250°. The acid coming over between 190° and 200° was collected apart to be examined by saturation.

50 grs. of the acid which remained in the retort boiling at 250° were then examined, and found to require 31·20 grs. of carbonate of soda in the first experiment, and 31·07 in the second, for saturation; the mean of the two experiments would correspond to 63·11 per cent. of nitric acid.

50 grs. of the most volatile portion, namely, that which came over between the temperatures of 190° and 200°, were then weighed out exactly; this quantity was found to require no less than 41·92 grs. in the first experiment, and 41·91 in the second, corresponding to 84·96 per cent. nitric acid; but then it must be remembered that this acid had a very dark red colour.

A quantity of this red acid was introduced into the decolorizing apparatus, and a constant rapid stream of dry air made

to bubble through it for two hours; at the expiration of that time it was found to be perfectly limpid, and colourless as water, and to have a specific gravity of 1·516 at 60°.

50 grs. of the last acid were weighed out and neutralized with pure carbonate of soda as before. The numbers below will show the amount required for saturation:—

| Exp. | Carb. of soda. | Mean. |
|---|---|---|
| 1. . . | 41·77 | 41·70, corresponding to 42·27, or 84·54 per cent. nitric acid. |
| 2. . . | 41·69 | |
| 3. . . | 41·64 | |

This acid began to boil at about 184°, the greater part distilling over between the temperatures of 184° and 188°; it afterwards rose when near the end to 200°.

The first portion that came over was collected apart, introduced into the decolorizing apparatus, and dry air again drawn through it until it was quite colourless. This was found to be necessary after each distillation, on account of the decomposition that it suffered upon boiling, which rendered it as dark in colour as the original acid. 50 grs. of the colourless acid, of the specific gravity of 1·517 at 60°, were weighed out, and carbonate of soda very carefully added until neutral to test-paper. The increase in the specific gravity this time only amounted to ·001.

| Exp. | Carb. of soda. | | Acid. | Mean. |
|---|---|---|---|---|
| 1. . . | 41·79 | = | 42·36 | 42·37. |
| 2. . . | 41·81 | = | 42·38 | |

Hence in 100 parts—

| | | According to theory with 1 eq. water. | |
|---|---|---|---|
| Real acid . . | 84·74 | Real acid . . | 85·71 |
| Water . . . | 15·26 | Water . . . | 14·28 |
| | 100·00 | | 99·99 |

This would give, when compared with the theoretical composition of nitric acid with 1 equiv. of water, a deficiency of ·97 in the acid, and an excess of ·98 in the water.

This hydrate, when pure, was a perfectly limpid and colourless liquid, like so much water; it boiled at 184°, and had a specific gravity of 1·517 at 60°. It was found not to have the slightest action on tin or iron even when boiled. A portion of this acid placed in a freezing mixture composed of ice and salt suffered no change.

These experiments leave little doubt concerning the composition of the first hydrate of nitric acid, namely, that it is the true mono-hydrate, consisting of 1 equiv. of nitric acid and 1 of water, $HO, NO_5$.

*Deuto-Hydrate.*—In preparing this hydrate, I set out by obtaining a quantity of colourless strong nitric acid, the exact amount of real acid in which was ascertained by saturation to

be 79·79 per cent. To reduce this acid to the proper strength, so as to contain exactly 2 equivs. of water, it was found by calculation that it would require 63·86 grs. of water to every 1000 grs. of acid.

The proper proportions of acid and water were weighed out carefully in a stoppered specific gravity bottle, and the two mixed. This mixture was cooled down to 60° and found to have the sp. gr. 1·486.

50 grs. of this hydrate were weighed out and saturated in the usual way with recently-ignited carbonate of soda. The quantities of carbonate of soda required were as follows:—

| Exp. | Carb. of soda. | Mean. |
|---|---|---|
| 1. . . | 37·45 | 37·49, or 74·98 per cent. acid. |
| 2. . . | 37·53 | |

An acid containing 2 equivs. of water will contain 75 per cent. real acid.

A portion of this acid was introduced into a small retort and distilled. It began to boil, as nearly as could be judged, at about 200°, it being difficult to come at the exact temperature on account of the very rapid rise of the thermometer, which continued to take place until it had gained the temperature of 218°; it afterwards rose when near the end to 250°.

It appears, then, from these experiments, that no such thing as a deuto-hydrate exists, but that when a mixture is made in the proportions to form such a hydrate and subjected to distillation, it divides spontaneously into the first and another, at the same time suffering considerable decomposition; and the acid which is found remaining in the retort has the exact boiling-point of the tetra-hydrate, namely, 250°; and moreover, the first portion that came over had the exact density of the first.

A portion of this acid placed in a freezing mixture of ice and salt, suffered not the least solidification.

*Tetra-Hydrate.*—This hydrate was prepared in the same way as the first, namely, by preparing a quantity of colourless acid, ascertaining its saturating power, and mixing it with the proper quantity of distilled water, ascertained by calculation. It was then tried afterwards by saturation to see if it was correct; the numbers below will show the difference:—

| Exp. | Carb. of soda. | | Acid. | Mean. |
|---|---|---|---|---|
| 1. . . | 29·96 | = | 30·37 | 30·32, or 60·64 per cent. real acid. |
| 2. . . | 29·87 | = | 30·27 | |

| | | According to theory with 4 eqs. water. | |
|---|---|---|---|
| Real acid . . | 60·64 | Real acid . . . | 60 |
| Water . . . | 39·36 | Water . . . . | 40 |
| | 100·00 | | 100 |

The acid had a density of 1·424 at 60°; it began to boil at 250°, and distilled over perfectly colourless and unchanged; towards the end, when slight decomposition commenced, the temperature rose to 260°.

Five or 6 ounces of very weak acid, of the density of 1·180, were introduced into a retort and kept heated just below its boiling-point for two or three hours; the heat was increased from time to time so as to make it boil briskly, and a thermometer introduced through the tubulure; when that which remained in the retort boiled uniformly at 250°, the heat was withdrawn and it was allowed to cool.

When the specific gravity of this acid was taken, it was found to be close upon that of the tetra-hydrate, but not exactly; probably if I had operated upon a large quantity, and carried it on for a longer time, it would have been more so; as found, its density was 1·412 instead of 1·424, which would make a difference of rather less than $1\frac{1}{2}$ per cent. deficiency in the acid.

This is, I have no doubt, the proper hydrate of nitric acid, $HO, NO_5 + 3HO$, as it is generally considered; and as Dr. Dalton correctly observed, acids which are either stronger or weaker than this acid, are brought to this strength by continued ebullition, the former losing acid and the latter water.

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## CC. *On the Products of the Decomposition of Cuminate of Ammonia by Heat.* By Mr. Frederick Field.

THE peculiar mode of decomposition which the ammonia salts of inorganic acids exhibit when exposed to the action of heat, occurs likewise in the ammonia compounds of organic acids, although the results in the latter instances are usually of a more complicated nature. In most of these cases a formation of water takes place, the hydrogen of which is derived from the volatile alkali, while the acid furnishes the oxygen, the residue of which combines in a more intimate manner with the nitrogen of the ammonia. In decompositions, however, of *inorganic* compounds this reduction seems to be carried at once as far as it can go, the whole of the hydrogen contained in the ammonia being converted into water; while in *organic* salts this hydrogen is eliminated only by degrees, an intermediate body being produced between the original ammonia salt and the final product of the decomposition. Thus we find that nitrite and nitrate of ammonia, when exposed to heat, are at once converted into water, and respectively into nitrogen and nitrous oxide. Oxalate of ammonia,

on the other hand, if submitted to a gentle heat, loses only two equivalents of water, the residue of both base and acid combining to form oxamide, and only by a strong and brisk application of heat Dœbereiner converted it into cyanogen, the rest of the hydrogen being eliminated in the form of water.

The dry distillation of oxalate of ammonia thus affords the prototypes of two series of compounds, which may arise from ammoniacal salts by the elimination of two or four equivalents of water respectively. There are few cases, however, in which the decomposition of ammoniacal salts have been carefully studied, and the instances in which we are acquainted with the representative of the two types are exceedingly scarce. We are indeed intimate with a very great number of amidogen compounds analogous to oxamide (fumaramide, salicylamide, succinamide, anisylamide, &c.), but only few of these have been obtained from ammoniacal salts by the action of heat. The greatest number of these bodies were produced by the change most compound æthers suffer under the influence of ammonia, a beautiful mode of decomposition pointed out first by Professor Liebig in the transformation of oxalate of ethyl into oxamide, or by the action of gaseous ammonia on other substances related in some manner with the acid: thus was chloride of benzoyle converted into benzamide by Wöhler and Liebig, and lately lactide into lactimide by Pelouze.

As yet, however, the members of the second class, those compounds standing to other acids in the same relation as cyanogen to oxalic acid, are very rare. From a beautiful experiment of Pelouze, we know that the vapour of formiate of ammonia, when passed through a red-hot tube, is converted into water and hydrocyanic acid. In their investigation on the radical of benzoic acid, Wöhler and Liebig obtained a peculiar oil by the action of heat on benzamide, which at that time they did not study more closely. The same body was at a later period obtained in the dry distillation of benzoate of ammonia, and fully examined by Fehling, who found that this interesting substance, to which he gave the name *benzonitrile*, has the composition $C_{14} H_5 N$, and is produced from benzoate of oxide of ammonium, exactly in the same manner as cyanogen and prussic acid are formed respectively from oxalate or formiate of ammonia. These facts did not long remain isolated. Schlieper, in an excellent examination he has lately published on the products of oxidation of gelatine by chromic acid, discovered that in these reactions, among other products, the body $C_{10} H_9 N$ is formed, valeronitryle or valerianate of ammonia—4 equivs. of water.

The members of this class acquire every day a greater degree of importance. A remarkable paper, read before the

Chemical Society a short time since by Dr. Kolbe and Mr. Frankland, has indeed opened a most interesting connexion between these bodies and another class of substances, which hitherto have been obtained by very different processes. The conversion of cyanide of ethyl into metacetonic acid by means of alkalies and acids, seems to indicate that cyanide of ethyl is nothing else than metacetonitryle. This experiment is likely to be of great importance, for it is exceedingly probable that the whole class of substances alluded to must be considered as a class of cyanogen compounds. It is evident that similar considerations may be applied to cyanide of methyl and cyanide of amyl, lately described by Balard; and the conversion of these cyanides respectively into acetic and capronic acids, which we have a right to anticipate on treating them with alkalies or acids, will prove that these compounds are the nitriles of acetic and capronic acids—acetonitryle and capronitryle—which as yet have not been obtained by the action of heat on the ammoniacal salts of these acids.

The following experiments on the action of heat on cuminate of ammonia have been made with the hope of contributing to the history of the nitryles, or organic cyanides, as they perhaps should be more correctly designated.

The cuminic acid employed in my experiments was prepared by the action of solid hydrate of potash on oil of cumin, and the product perfectly freed from the least traces of cymol which it might possibly contain by precipitating the potash salt by hydrochloric acid, dissolving the precipitated cuminic acid in ammonia, reprecipitating by hydrochloric acid, and crystallizing from water. The acid was then dissolved in strong ammonia, and the solution subjected to heat. The first portions which passed over, although consisting chiefly of water and ammonia, together with cuminate of ammonia, which is always carried over with the steam, presented more or less an opalescent appearance, indicative of traces of the oil. On evaporating the solution in the retort to dryness, a portion of the salt is decomposed, ammonia is evolved, and cuminic acid condenses in beautiful plates upon the sides and neck of the retort, separation going on even on raising the temperature; but simultaneously another decomposition takes place, water is eliminated, in consequence of which there are produced a peculiar white crystalline body, difficultly soluble in water, and subsequently a colourless oil of a most fragrant odour; although the operation may seem very simple, experience alone teaches the proper regulation of temperature necessary to obtain these two bodies.

*Cuminamide.*—Observing in my first experiments evolution of ammonia and sublimation of cuminic acid on heating cu-

minate of ammonia, I thought that by heating it under pressure, the ammonia then not being able to escape, the desired change might be effected. Accordingly a portion of the salt was placed in a strong glass tube, and after sealing the other end, gradually heated in an oil-bath to nearly the boiling-point of the oil, and allowed to cool. On cooling the mass appeared to have been completely fused, but perfectly solid and of a highly-crystallized texture. On examination it was found to be insoluble in cold water and ammonia, but very soluble in hot water, from which it solidified into a crystalline mass as the temperature cooled; this alone sufficiently indicated that a complete change had been effected, the cuminate of ammonia being readily soluble in cold water. In order to ascertain the nature of the change it was dissolved in hot water, and weak ammonia added to dissolve any cuminic acid that might be mixed with it, and crystallized; the crystals were separated by filtration, and once more dissolved in a hot weak solution of ammonia, from which they separated on cooling in brilliant white crystalline plates, similar in appearance to benzamide. These were dried at 212° in a water-bath, and analysed in the usual manner.

I. 0·174 grm. of substance burnt with oxide of copper yielded 0·470 of carbonic acid and 0·128 of water.

II. 0·248 grm. yielded 0·670 of carbonic acid and 0·181 of water.

III. To estimate the nitrogen, 0·287 grm. ignited with soda-lime yielded 0·390 of ammonio-chloride of platinum*.

From these analytic results the following per-centages are obtained:—

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . | 73·66 | 73·67 | |
| Hydrogen . | 8·17 | 8·10 | |
| Nitrogen . | | | 8·50 |

leading to the formula $C_{20}H_{13}NO_2$, as may be seen from the following comparison of the theoretical and experimental numbers:—

| | | | Theory. | Mean of exp. |
|---|---|---|---|---|
| 20 equivs. | of Carbon . . | 120 | 73·68 | 73·66 |
| 13 | ... Hydrogen . | 13 | 7·99 | 8·13 |
| 1 | ... Nitrogen . | 14 | 8·52 | 8·50 |
| 2 | ... Oxygen . . | 16 | 9·81 | 9·71 |
| | | 163 | 100·00 | 100·00 |

This body therefore is cuminamide, $NH_2C_{20}H_{11}O_2$, having

* In this operation a large quantity of an oily body is produced, which floats on the surface of the hydrochloric acid. It is evidently *cumol*.

precisely the same relation to cuminate of ammonia as oxamide to oxalate of ammonia.

In preparing large quantities of this substance the employment of close tubes would be very inconvenient, and I soon found that it could be obtained in a retort by the continued application of a heat sufficient to keep the salt in a state of semi-fluidity. The analyses II. and III. were made with the product obtained in this manner.

Cuminamide crystallizes like benzamide, in two forms, according to the state of the solution; if crystallized immediately, or from a strong solution, it separates in the form of crystalline tables of great brilliancy, but if the solution be dilute, it crystallizes after the lapse of some hours in long opake needles, both forms having exactly the same composition. It is soluble in hot and cold alcohol in any proportion, as also in æther. This new amide differs from most others that have been described in remaining intact on the addition of strong solution of potash, or mineral acids; from the former it crystallizes in large plates after some days. Long boiling with alkalies or acids is scarcely sufficient to produce the characteristic conversion of amides either into ammoniacal salts or combinations of the base with the acid and evolution of ammonia.

*Cumonitrile.*—On heating cuminate of ammonia until it is perfectly fused, and keeping the fused mass in a state of brisk ebullition, large globules of a light yellowish oil pass over with water, evidently derived from the decomposition of the salt; when the globules began to diminish the process was stopped, the oil was separated from the water in the receiver by means of a pipette, the remaining distillate added to the mass in the retort, and the process again repeated as before; in this manner, after some half-dozen distillations, nearly an ounce of oil was obtained; it was well-washed with ammonia to remove cuminic acid, which seemed to be soluble in the oil, then treated with hydrochloric acid to remove ammonia, thoroughly washed with water, and digested with chloride of calcium; after standing some days to separate chloride of calcium, it was distilled and carefully rectified, the first portions being rejected, as possibly containing traces of water; the middle portion was reserved and placed in a retort with a coil of platinum; the liquid entered into ebullition at 239° C., at which point it remained stationary while at least a quarter of an ounce was passing over. This portion was employed in the following analyses:—

I. 0·212 grm. burnt with oxide of copper yielded 0·644 of carbonic acid and 0·145 of water.

II. 0·225 grm. yielded 0·6835 of carbonic acid and 0·161 of water.

III. 0·244 grm. ignited with soda-lime yielded 0·364 of ammonio-chloride of platinum*.

From these analytical results the following per-centages are obtained:—

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . | 82·82 | 82·84 | |
| Hydrogen . | 7·59 | 7·96 | |
| Nitrogen . | | | 9·34 |

leading to the formula $C_{20} H_{11} N$, as may be seen from the following comparison of the theoretical and experimental numbers:—

| | | Theory. | Mean of exp. |
|---|---|---|---|
| 20 Carbon . . | 120 | 82·76 | 82·83 |
| 11 Hydrogen . | 11 | 7·58 | 7·77 |
| 1 Nitrogen . | 14 | 9·66 | 9·34 |
| | 145 | | |

This body is therefore cumonitrile, $C_{20} H_{11} N$, standing in the same relation to cuminate of ammonia as cyanogen does to oxalate of ammonia.

Cumonitrile is a perfectly clear and colourless liquid, possessing a high refractive power; it has a most powerful and agreeable odour and a burning taste; it is somewhat soluble in water, causing turbidity in that liquid; it is soluble in all proportions of alcohol and æther; it is lighter than water, having a specific gravity 0·765 at 14° C. (57° Fahr.). The boiling-point, when in contact with metal, is constant at 239° C. (462·2° Fahr.), at the barometric pressure 0·7585 m. = (29·85 inches). The equivalent of cuminic acid containing $3C_2 H_2$ more than the equivalent of benzoic acid, it was interesting to compare the boiling-points of benzonitrile and cumonitrile. According to Fehling's experiments, the boiling-point of benzonitrile is 191° C.; on calculating from this observation the boiling-point of cumonitrile according to the rules first pointed out by Kopp, the boiling-point should be $191 + 3 \cdot 19 = 248$.

Dr. Fehling does not however mention that he had this substance in contact with metal, and it is not improbable that the true boiling-point of benzonitrile is somewhat lower; the vapour of cumonitrile is very inflammable and burns with a bright flame, which deposits much carbon.

* Professor Fehling found it difficult to estimate the nitrogen in benzonitrile in the form of ammonia, drops of oil passing over in the hydrochloric acid. In the case of cumonitrile, this method gave very accurate results; oil drops also passed over, but were evidently *cumol*.

The strongest nitric acid has but little action upon this substance; after boiling, however, and setting aside for some days, crystals of cuminic acid are formed. On being heated with potassium it darkened, and apparently another oil was produced; the mass on being washed and tested for cyanogen in the usual manner gave a copious precipitate of prussian blue, which seems to be strongly in favour of the view which Kolbe and Frankland have recently promulgated. A strong alcoholic solution of potash has no immediate action on cumonitrile, but after a day or two, on pouring the liquid into a watch-glass, it partially solidified into a yellow crystalline mass, a mixture of the original substance with white crystals. These crystals after purification had all the appearance of cuminamide, and in order to be satisfied of their composition—

I. 0·174 grm. burnt with oxide of copper yielded 0·472 of carbonic acid and 0·124 of water; the calculated per-centage of carbon and hydrogen from these numbers being—

| | |
|---|---|
| Carbon . . | 73·62 |
| Hydrogen . | 7·91 |

These numbers correspond to those of cuminamide, as may be seen by a comparison with the former analyses.

It appears then that cumonitrile, on the addition of potash, is not, as might have been expected, converted into cuminate of ammonia, but into cuminamide, taking 2 instead of 4 atoms of water—$C_{20}\,H_{11}\,N + 2HO = C_{20}\,H_{13}\,NO_2$, the latter body being, as before remarked, in such a remarkable degree unaffected by alkalies or acids.

Having obtained one amide with comparative ease, many other ammoniacal salts were heated for the purpose of obtaining analogous amidogen compounds. Benzoate of ammonia was tried unsuccessfully, and it appears from the account published by Fehling of his investigation of benzonitrile, that the residue in the retort consisted entirely of benzoate of ammonia, that salt appearing to have lost directly 4 equivs. of water without undergoing an intermediate conversion into an amide by the loss of 2 equivs. Nitrobenzoic acid was dissolved in ammonia, evaporated, and cautiously fused for a considerable time; when cold it was found to be insoluble in water and ammonia at the ordinary temperature, but dissolved by hot water, from which it crystallized in beautiful yellow needles. On analysis, the following results were obtained:—

I. 0·222 grm. of substance burnt with oxide of copper yielded 0·410 of carbonic acid and 0·080 of water.

II. 0·255 grm. yielded 0·472 of carbonic acid and 0·087 of water.

From these results the following per-centages were obtained:—

| | I. | II. |
|---|---|---|
| Carbon . . . | 50·36 | 50·43 |
| Hydrogen . . | 4·00 | 3·78 |

corresponding to the formula $C_{14} H_6 N_2 O_6$, as may be seen from the comparison of the theoretical and experimental numbers:—

| | | | | Theory. | Mean of exp. |
|---|---|---|---|---|---|
| 14 equivs. | of | Carbon . . | 84 | 50·60 | 50·39 |
| 6 | ... | Hydrogen . | 6 | 3·62 | 3·98 |
| 2 | ... | Nitrogen . | 28 | 16·87 | |
| 6 | ... | Oxygen . . | 48 | 28·91 | |
| | | | 166 | 100·00 | |

This body is therefore nitrobenzamide, having the same relation to nitrobenzoate of ammonia as cuminamide has to cuminate of ammonia.

This beautiful substance can only be obtained with difficulty, as the nitrobenzoate of ammonia explodes violently unless very great caution is employed.

A specimen of chlorobenzoic acid, made in the laboratory for some other investigation, was dissolved in ammonia and heated; it fused readily, became perfectly insoluble in cold water and ammonia, but soluble in hot water, crystallizing as the solution cooled in long needles of great beauty. The specimen of acid afforded me, being all that could be spared, was insufficient for the manufacture of an amide; I prepared a portion of chlorobenzoic acid by acting upon benzoic acid for some days with hydrochloric acid and chlorate of potash; after purification it was burnt with chromate of lead and gave the following results:—

I. 0·394 grm. = 0·769 of carbonic acid and 0·114 of water.

From this result the following per-centage was obtained:—

| | Experiment. | Theory. |
|---|---|---|
| Carbon . . . | 53·22 | 53·61 |
| Hydrogen . . | 3·22 | 3·25 |

leading to the formula $HO, C_{14} \left\{ \begin{matrix} H_4 \\ Cl \end{matrix} \right\} O_3$, 1 equiv. of the hydrogen of benzoic acid replaced by an equivalent of chlorine.

This acid, however, on being subjected to the usual treatment by solution in ammonia and subsequent heat, did not fuse but blackened, charcoal being separated. Unfortunately the specimen of ammoniacal salt from which I had made the former compound was not analysed, probably it would have

proved to be $C_{14}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right\}O_3, HO$, or $C_{14}\left\{\begin{matrix}H_2\\Cl_3\end{matrix}\right\}O_3, HO$, a dichlorobenzoic or a trichlorobenzoic acid, such existing.

These experiments were conducted in the laboratories of the Royal College of Chemistry under the direction of Dr. Hofmann, to whom I beg to offer my best thanks for his advice and assistance during their progress.

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## CCI. *Contributions to the Chemical History of Gun-Cotton and Xyloidine.* *By* Mr. John Hall Gladstone, *of University College, London.*

AT the commencement of the present year, having perceived that considerable doubt rested on the ultimate composition of gun-cotton, I undertook a series of experiments with a view to ascertain it, if possible; and during my investigation my attention was drawn to various papers that appeared on the subject, where I found contradictory accounts, not only of the results of analysis, but also of the action of various reputed solvents. The experiments detailed below, although they are far from exhausting the subject, may serve to explain some of these anomalies, and to point out a few facts, which, as far as I have been able to learn, have not been hitherto noticed.

The cotton employed was that used by jewellers, well-carded, perfectly white, and free from imperfections. An analysis of the substance by combustion with oxide of copper in a stream of oxygen yielded the following results:—

| | |
|---|---|
| Cotton employed . . . . . | 3·16 grs. |
| Carbonic acid produced . . . | 5·14 ... |
| Water produced . . . . . | 2·06 ... |

These proportions are,—

| | |
|---|---|
| Carbon . . . | 44·37 |
| Hydrogen . . | 7·24 |
| Oxygen . . . | 48·39 |
| | 100·00 |

Lignine calculated from the formula $C_{24}H_{20}O_{20}$:—

| | |
|---|---|
| Carbon . . . | 44·44 |
| Hydrogen . . | 6·17 |
| Oxygen . . . | 49·39 |
| | 100·00 |

The excess of hydrogen doubtless arises from moisture absorbed by the oxide of copper during the unavoidable delay in mixing it with the cotton.

This cotton, which may be considered as pure lignine, was steeped until thoroughly wetted in a mixture of nitric acid of spec. grav. 1·502, and nearly an equal bulk of strong sulphuric acid, then well-washed with water, and dried at a temperature not exceeding 212°. In one instance 38·38 grs. of cotton became 66·84 grs., being an increase of 28·46 grs., or 74·15 per cent. In a second experiment 59·3 grs. of cotton gave an increase of 43·7 grs., or 73·7 per cent. The gun-cotton, or pyroxyline, thus produced resembled the original cotton in physical properties very closely, and exploded at about 370°, producing no smoke and leaving no residue.

The action of various solvents and reagents upon this substance was found to be as follows:—It is absolutely insoluble in pure water, and nearly so in strong alcohol, æther, whether hydrated or anhydrous, and in a mixture of æther with $\frac{1}{10}$th part of alcohol; but acetic æther instantly destroys its fibre, and dissolves it in large quantity. The solution yields on spontaneous evaporation a white powder of the same weight as the original pyroxyline, but I have found it very difficult to drive off the last traces of the solvent. The action of sulphuric acid upon it differs from that exerted upon unaltered cotton; for, while the latter is instantly dissolved by the strong acid, and charred upon a slight elevation of temperature, pyroxyline dissolves with difficulty unless the acid be warmed, evolving at the same time nitric oxide and other gases, and not being charred even upon boiling. With the aid of heat it dissolves immediately in a solution of potash. By means of these three last-mentioned tests I was able to prove the absence of any unaltered cotton in the product under examination. The action of other reagents upon gun-cotton was not so decided; it was dissolved, but not without long boiling, by ammonia, the alkaline carbonates, hydrochloric acid, acetic acid, both glacial and dilute, and weak sulphuric acid. These solutions, as well as the two preceding, contained nitric acid; nothing could be precipitated from them by dilution or neutralization; and when evaporated they yielded only a dark brown amorphous matter. It is evident that none of these reagents restore the lignine in its original condition; and they do not afford any means of ascertaining whether the compound contains the elements of nitric or hyponitric acid.

As there exists a great discrepancy in the accounts given of the increase of weight in making gun-cotton, I examined whether the length of time it was immersed in the acid liquor, or the proportions of the acids employed, were the cause. The length of immersion I found to produce no alteration; but

upon employing two measures of sulphuric acid to one of nitric acid, I obtained a product resembling in all respects ordinary pyroxyline, yet 42·77 grs. gave an increase of only 24·31 grs., or 56·84 per cent. Upon a repetition of this experiment I found the increase to be 59·93 per cent., and again 70·6 per cent. Suspecting from the disparity of these results that something might be dissolved in the acid liquor, I immersed 6·7 grs. of cotton in a large quantity of the mixed acids, but it increased 4·9 grs., or 73·1 per cent. Perceiving that I had obtained an opposite effect to that anticipated, I treated 12·64 grs. of cotton with just sufficient of the mixture to wet it thoroughly: the fibre was evidently somewhat destroyed; the increase in weight was only 6·54 grs., or 51·74 per cent., and the acid liquor squeezed from the cotton, neutralized with ammonia, evaporated to dryness, and heated, gave abundant evidence of organic matter being present. Lest however it might be supposed that the whole had not been converted into pyroxyline, it was treated again with the mixed acids, but that produced an increase of only 0·12 gr. The action of various solvents confirmed its identity with ordinary pyroxyline, while its solubility in potash proved that the transformation had been very nearly complete. A repetition of the experiment gave similar results. It thus appears that the small increase in weight in the preparation of pyroxyline takes place when there is not sufficient nitric acid present to prevent the peculiar action of the sulphuric acid, namely, that of dissolving and altering it. When however the increase amounted to about 74 per cent., I was never able to detect the presence of oxalic acid or other organic matter in the acid liquor; and as no gas is evolved during the preparation of pyroxyline, it may be concluded that there is no secondary product containing carbon.

Subsequently, when Dr. Schönbein had specified *his* method of making gun-cotton, I treated 18·78 grs. of cotton with a mixture of three parts of sulphuric acid and one of nitric acid, sp. gr. 1·5, following his directions. The result was 32·92 grs. of a substance similar to that produced in former experiments, being an increase of 75·20 per cent. On another occasion 80·95 grs. of cotton gave an increase of 61·10 grs., or 75·47 per cent. The action of solvents and reagents confirmed the identity of this pyroxyline with that obtained in my previous experiments, and I was equally able to establish the absence of any secondary product containing carbon.

In determining the ultimate composition of pyroxyline several precautions were found to be necessary. In the ana-

lyses recorded below it was cut into small pieces, and, after the weight was taken, mixed carefully with oxide of copper. To prevent its caking together the admixture of a little asbestos was found useful. This was introduced into a long combustion-tube, then some fresh oxide of copper, and upon it again some fused into lumps so as to fill the whole bore for about 7 inches. Lastly, was added a mixture of copper turnings and reduced copper for about 9 inches. The combustion conducted cautiously in the usual manner gave the following results; the pyroxyline burnt in the sixth experiment having been prepared by Schönbein's method.

| | I. | II. | III. | IV. | V. | VI. |
|---|---|---|---|---|---|---|
| Pyroxyline employed | 4·09 | 4·61 | 3·57 | 4·85 | 4·55 | 2·905 |
| Carbo. acid produced | 4·20 | 4·52 | 3·42 | 4·88 | ... | 2·84 |
| Water produced . . | 1·19 | 1·36 | ... | ... | 1·34 | 0·87 |

Hence in 100 parts,—

| | I. | II. | III. | IV. | V. | VI. |
|---|---|---|---|---|---|---|
| Carbon . | 27·90 | 26·74 | 26·10 | 27·44 | ... | 26·65 |
| Hydrogen | 3·22 | 3·27 | ... | ... | 3·27 | 3·32 |

In order to determine the amount of nitrogen the differential mode was adopted, as the method of MM. Will and Varrentrapp is inapplicable to substances containing this element in so highly oxidized a state. The same precautions were taken as in the estimation of carbon; and the collected gases gave the following results after due correction for barometrical pressure :—

| | I. | II. | Another specimen. |
|---|---|---|---|
| Carbonic acid . | 25·0 | 38·5 | 23·9 |
| Nitrogen . . . | 5·5 | 8·5 | 5·1 |

These proportions are,—

| Nitrogen. | | Carbonic acid. |
|---|---|---|
| 1 | : | 4·55 |
| 1 | : | 4·53 |
| 1 | : | 4·68 |

The volumes of the gases represent respectively equivalents of carbon and nitrogen, and since no secondary product is formed in the conversion of lignine into pyroxyline, the 24 equivalents of carbon in the former must be found in the latter. This will give the following ratio in equivalents of carbon and nitrogen according to the three experiments above cited :—

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . . . | 24·0 | 24·0 | 24·0 |
| Nitrogen . . . | 5·28 | 5·3 | 5·12 |

or 24 : 5, which accords with the proportions assigned by M. Pelouze *.

The formula which best agrees with these results is the following:—$C_{24}\left\{\begin{matrix}H_{15}\\5\,NO_4\end{matrix}\right\}O_{20}$, which reckoned to 100 parts, gives—

| | |
|---|---|
| Carbon . . . . . | 26·23 |
| Hydrogen . . . . . | 2·73 |
| Nitrogen . . . . . | 12·75 |
| Oxygen . . . . . | 58·29 |

In order to compare pyroxyline with xyloidine, I treated starch with fuming nitric acid until the whole was converted into a gelatinous mass. The addition of water then threw down a white powder, which was subsequently well-washed and dried. The iodine test proved the absence of all unaltered starch. The xyloidine thus obtained explodes at about 360°, leaving a carbonaceous residue. It is slightly soluble in æther, with which it is capable of forming a peculiar compound not yet investigated; more so in alcohol, but most of all in æther mixed with a small proportion of alcohol, or in acetic æther. It is dissolved by strong sulphuric acid without the aid of heat, and by boiling solutions of potash, ammonia, hydrochloric acid and dilute sulphuric acid. These solutions contain nitric acid, and nothing is precipitated from them by dilution or neutralization. Xyloidine is also soluble in strong acetic acid, or in nitric acid, whether fuming or of sp. gr. 1·25, but is reprecipitated from either by dilution.

It was also found that nitric acid of ordinary strength (sp. gr. 1·45) answered equally well in the preparation of this substance; but when acid of sp. gr. 1·41 was employed no such result was obtained. Starch treated with a mixture of equal measures of nitric and sulphuric acids produced a substance of greater combustibility, and more closely resembling pyroxyline, but differing from it in being soluble in glacial acetic acid, and in a mixture of æther with one-tenth part of alcohol, as also in the action that acetic æther exerts upon it. Xyloidine also when subjected to the mixed acids gave a product identical with the above, as far at least as the action of solvents can prove.

Xyloidine burnt by means of oxide of copper, with the usual precautions, gave the following results. The substance employed in the third experiment was made from arrow-root.

* *Comptes Rendus*, Jan. 4.

| | I. | II. | III. |
|---|---|---|---|
| Xyloidine employed . . | 4·77 | 5·23 | 6·75 |
| Carbonic acid produced . | 5·30 | 5·91 | 7·87 |
| Water produced . . . | 1·84 | 1·96 | 2·80 |

Hence in 100 parts,—

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . | 30·30 | 30·82 | 31·79 |
| Hydrogen . | 4·28 | 4·16 | 4·60 |

In the determination of nitrogen by the differential method the proportions of the gases obtained were,—

| | I. | II. | III. |
|---|---|---|---|
| Carbonic acid . | 70·7 | 53·4 | 53·8 |
| Nitrogen . . . | 10·6 | 6·9 | 8·0 |

These are in the proportion of—

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . | 24·0 | 24·0 | 24·0 |
| Nitrogen . . | 3·59 | 3·10 | 3·57 |

These numbers suggest the simple substitution product $C_{24}\left\{\begin{matrix}H_{17}\\3NO_4\end{matrix}\right\}O_{20}$, in which the per-centage of carbon would be 31·37, and of hydrogen 3·70; yet the amount of nitrogen is somewhat too great, and there is far from being sufficient evidence to prove the definiteness of the substance itself. The wide difference also in the results obtained by various chemists can scarcely be accounted for, except upon the supposition that they have operated upon very different substances.

The solubility of xyloidine in nitric acid led me to examine whether any alteration could be effected upon pyroxyline by similar means. The most dilute acid which I found to have any effect upon it in the cold was that of sp. gr. 1·414; but the alteration took place by means of this only after long standing, and but to a slight extent. Nitric acid of sp. gr. 1·45 however is capable of dissolving pyroxyline, and alters both its composition and properties, as will be presently described; whilst fuming nitric acid has not the slightest effect upon it. The new product just mentioned is acted upon somewhat differently by various solvents, according to whether it exists in a fibrous condition, or in powder as precipitated from solution; yet I have found by experiment that no alteration in weight is effected by this change of condition. When in fibre it is slightly soluble in strong alcohol, æther, a mixture of æther with one-tenth part of alcohol, and acetic æther; but when in the pulverulent state it is very soluble in these menstrua, and in glacial acetic acid. In either con-

dition it leaves a carbonaceous residue on combustion, is dissolved by nitric acid, whether of sp. gr. 1·25 or 1·5, and reprecipitated upon dilution. Strong sulphuric acid also dissolves it in the cold, and chars it at a temperature below 180°. These two last properties show that the original pyroxyline was perfectly free from admixture with this new substance.

There occurs a considerable decrease of weight through this transformation. In the first experiment 32 grs. of substance operated upon gave 25·82 grs. of the new product; in the second 43·64 grs. of the one yielded 34·68 of the other. Now assuming the increase in the preparation of pyroxyline to be 75 per cent., the weight of the new product above that of the original cotton would be, as calculated from these figures, 41·1 and 39·05 per cent.

When this new product, whether in the fibrous or the pulverulent condition, was treated with a mixture of equal parts of nitric and sulphuric acids, it increased considerably in weight, and the resulting substance had all the properties of pyroxyline as prepared in the usual manner. 11·16 grs. of the one yielded 13·56 grs. of the other; the quantity that should theoretically have been obtained, calculating it from the decrease in making the new product, is 13·84 or 14·04 grs. Again, 12·35 grs. of the substance as precipitated from solution gave 15·75 grs., the theoretical amount would have been 15·31 or 15·54 grs. This result proves the distinctness of the new product from xyloidine, a fact that could not have been ascertained from the action of the before-mentioned solvents.

Whilst engaged in obtaining these results, I also examined the action of nitric acid of various degrees of strength upon pure cotton. By treating it with nitric acid of sp. gr. 1·5 I obtained a product evidently different from gun-cotton, but as it did not appear to be homogeneous throughout, I passed on to investigate the action of a weaker acid. That of sp. gr. 1·45 gave a substance which proved to be identical with the product of the action of the same acid upon pyroxyline. Upon a repetition of the experiment 68·54 grs. increased in weight 14·61 grs., or 21·31 per cent.—a smaller increase than might have been anticipated, but which may easily be accounted for by the fact that the whole cotton had not been transformed, as was proved by a considerable portion being left undissolved by a boiling solution of potash. Nitric acid of sp. gr. 1·414 produced the same alteration, but only to a small extent, and after long standing. 23·75 grs. of cotton soaked in nitric acid of sp. gr. 1·516 became a hard mass,

and increased in weight 13·49 grs., or 56·8 per cent.; the action of various solvents upon the resulting substance indicated that it was a mixture of pyroxyline and the new product. On another occasion, when the transformation by means of nitric acid sp. gr. 1·47 proved to be complete, 29·52 grs. of cotton increased 9·51 grs., or 32·89 per cent. But in order to obtain a substance sufficiently pure for analysis 16·29 grs. of cotton were treated with enough nitric acid to dissolve the whole; the new product was precipitated by dilution, and the increase in weight was found to be 5·34 grs., or 32·78 per cent. In these instances there occurred a secondary product containing carbon not precipitable by water.

When this was subjected to combustion with oxide of copper, the following results were obtained:—

| | I. | II. | Another specimen. |
|---|---|---|---|
| Substance employed . | 3·15 | 2·985 | 3·165 |
| Carbonic acid produced | 3·58 | 3·39 | 3·55 |
| Water produced . . . | 1·00 | 1·01 | 1·14 |

Hence in 100 parts,—

| | | | |
|---|---|---|---|
| Carbon . | 30·99 | 30·97 | 30·59 |
| Hydrogen | 3·52 | 3·75 | 4·00 |

I was unable to obtain any very accurate estimation of nitrogen by the differential method: the results most to be depended upon were—

| | | |
|---|---|---|
| Carbonic acid . . | 120·7 | 76·7 |
| Nitrogen . . . . | 13·6 | 8·3 |

In the proportion of

| | | |
|---|---|---|
| Carbon . . . | 24·0 | 24·0 |
| Nitrogen . . . | 2·7 | 2·6 |

These numbers lead me to think that there are 3 equivalents of nitrogen in the compound, especially as I observed during the combustion that the substance became charred even 1 or 2 inches beyond the glowing charcoal, which will account for the deficiency of nitrogen when compared with the carbonic acid. Hence the composition of the new product coincides very nearly with that calculated from the formula $C_{24}\left\{\begin{matrix}H_{17}\\3NO_4\end{matrix}\right\}O_{20}$, namely,

| | |
|---|---|
| Carbon . . . . | 31·37 |
| Hydrogen . . . | 3·70 |
| Nitrogen . . . . | 9·15 |
| Oxygen . . . . | 55·78 |
| | 100·00 |

Under this supposition the increase in weight in the preparation would be 41·66 per cent.; very similar to that calculated from the results obtained by the action of nitric acid, sp. gr. 1·45, on pyroxyline, namely, 39·05 and 41·1 per cent.

In order to add an additional proof of the identity of the two substances obtained by the action of nitric acid of sp. gr. 1·45 on cotton and on pyroxyline, and also of the fact that pyroxyline is reproduced by the action of mixed sulphuric and nitric acids upon the new product, the experiment was repeated with a portion of the substance made from pure cotton: the result was pyroxyline. In the transformation 26·56 grs. became 38·04: now these 26·56 grs. were produced from 21·81 grs. of the original cotton; hence the increase upon the cotton itself would be 16·23 grs., or 74·4 per cent., coinciding with the amount usually obtained in the preparation of pyroxyline.

I. From these results it appears that in the treatment of woody fibre by nitric acid raised to its highest degree of strength by the addition of sulphuric acid, 5 equivalents of the acid combine with 1 of lignine to produce pyroxyline, displacing 5 equivalents of the elements of water, as indicated by the formula $C_{24}\left\{\begin{matrix}H_{15}\\5NO_4\end{matrix}\right\}O_{20}$. The amount per cent. of carbon and hydrogen hence deduced closely agrees also with that assigned by Mr. Ransome * and M. Pettenkofer †.

| | Calculated. | Ransome. | Pettenkofer. |
|---|---|---|---|
| Carbon . . | 26·23 | 26·28 | 26·26 |
| Hydrogen . | 2·73 | 3·16 | 2·75 |

In this case the synthetical experiment would give an increase of 69·44 per cent.—nearly the amount obtained in the best experiments. My own analyses however have yielded a somewhat larger amount of carbon.

II. If lignine be treated with nitric acid combined with more than 1 equivalent of water, another compound is produced, containing a smaller proportion of the elements of nitric acid, most probably $C_{24}\left\{\begin{matrix}H_{17}\\3NO_4\end{matrix}\right\}O_{20}$, and very closely resembling, but not identical with, pyroxyline.

$$C_{24}H_{20}O_{20}+3(NO_5,2HO)=C_{24}\left\{\begin{matrix}H_{17}\\3NO_4\end{matrix}\right\}O_{20}+9HO.$$

Also if pyroxyline itself be treated with nitric acid containing 3 equivalents of water, the same compound results:

* Phil. Mag., January 1847.

† *Pharmaceutisches Central Blatt*, Dec. 30th, 1846.

$$C_{24}\left\{\begin{matrix}H_{15}\\5NO_4\end{matrix}\right\}O_{20}+2(NO_5,3HO)=C_{24}\left\{\begin{matrix}H_{17}\\3NO_4\end{matrix}\right\}O_{20}+4(NO_5,HO).$$

And this transformation may be reversed.

Whilst completing my examination of this substance, my attention was drawn to the communication of M. Payen in the *Comptes Rendus* of Jan. 25th, where some properties of "coton hypoazotique" are described. It is possibly the same; yet, in order to express its distinctness from pyroxyline, I would propose as the appellation of my substance cotton-xyloidine.

Before concluding I would acknowledge my obligations to several chemists whose published investigations on the same subject have suggested many of my experiments, and more particularly to Professor Fownes for the valuable advice with which from time to time he has favoured me.

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## CCII. *On the Action of Nitric Acid on Cymol. First Part.* By H. M. Noad, *Esq.*

### *Formation of Toluylic and Nitrotoluylic Acids.*

WE possess in benzoic acid and its derivatives a well-defined group of substances connected in a variety of ways with a large number of organic families. These interesting bodies have been made subjects of investigation by several chemists. The study has been a fascinating one, and has resulted in a thorough development of their history, and of the products of their decomposition.

This group may be considered the prototype, as it were, of several parallel groups, presenting a very close relation with the composition of the benzoyl family. The careful study of the former has gradually made these known to us, in the same manner as the study of alcohol and its derivatives made us acquainted with several corresponding classes of bodies.

The methyl compounds, with which we have become familiar through the experiments of Dumas and Peligot* on pyroxylic spirit, and the amyl series, the origin of which we owe to the investigations of Cahours† on fusel oil, form two groups, the analogy of which with the alcohol series can be traced in every direction; they differ in composition from the former only by a multiple of $C_2H_2$, thus—

$HO, C_2H_3O$ = hydrated oxide of methyl.
$HO, C_4H_5O$ = hydrated oxide of ethyl.
$HO, C_{10}H_{11}O$ = hydrated oxide of amyl.

* Liebig's *Annalen*, xv. 1. † Ibid. xxx. 288.

The same relation is likewise observed in the acids resulting from the oxidation of these bodies, and these acids are perhaps even better adapted to point out this interesting regularity, as the gaps existing between the different alcohols are filled up in the series of the acids, which may be formed in a great variety of ways. A glance at the following table will render the regularity above alluded to at once obvious:—

| Alcohols. | Acids. |
|---|---|
| $HO, C_2 H_3 O$, pyroxylic spirit. | $HO, C_2 HO_3$, formic acid. |
| $HO, C_4 H_5 O$, alcohol. | $HO, C_4 H_3 O_3$, acetic acid. |
| | $HO, C_6 H_5 O_3$, metacetonic acid. |
| | $HO, C_8 H_7 O_3$, butyric acid. |
| $HO, C_{10} H_{11} O$, fusel oil. | $HO, C_{10} H_9 O_3$, valerianic acid. |
| | $HO, C_{12} H_{11} O_3$, caproic acid. |
| | $HO, C_{14} H_{13} O_3$, œnanthylic acid. |
| | $HO, C_{16} H_{15} O_3$, caprylic acid. |
| | $HO, C_{18} H_{17} O_3$, pelargonic acid. |
| | $HO, C_{20} H_{19} O_3$, capric acid. |
| &c. | &c. |

Now it seems that benzoic acid is a member of a similar series of acids, distinguished from each other by the same amounts of carbon and hydrogen, and that we may expect to find a representative of every single term of the benzoyl series in these other families. An examination of cumin oil by MM. Gerhardt and Cahours* has brought to light a new acid,—cuminic acid, $HO, C_{20} H_{11} O_3$, which exhibits a perfect analogy with benzoic acid, not only in its physical properties, but also in the metamorphoses which it undergoes when acted on by chemical agents. This acid is distinguished from benzoic, $HO, C_{14} H_5 O_3$, by containing $3(C_2 H_2)$ more; it stands to benzoic acid as valerianic acid stands to acetic acid, and when distilled with lime it is converted into cumol, $C_{18} H_{12}$, which represents benzol, $C_{12} H_6$, in the benzoyle series. The same investigation of cumin oil has made us acquainted with another carbo-hydrogen cymol, $C_{20} H_{14}$, which is also a representative of benzol in another series; but up to the present time the acid from which this carbo-hydrogen derives, and which would contain $4(C_2 H_2)$ more than benzoic acid, has not been discovered.

By the investigations of Pelletier and Walter† on the products of the distillation of resinous substances, of Deville‡ on the distillation of tolu balsam, and of Boudault and Glenard§ on the dry distillation of the dragon's blood, an addi-

* Liebig's *Annalen*, xxxviii. 67.
† Ibid, xxviii. 295.
‡ *Ann. de Chim. et Phys.* 3 sér. t. iii. p. 168.
§ *Journ. de Pharm. et de Chim.* 3 sér. t. vi. p. 250.

tion has been made to the number of carbo-hydrogens, and we have obtained knowledge of a new body, which was described by the first chemists under the name of retinaphtha, by the second under that of benzoène, and by the last under that of dracyl; for all three Berzelius* has proposed the more appropriate name of toluol† ($C_{14}$ $H_8$); this body, which differs from benzol in containing $C_2$ $H_2$ more, also represents that carbo-hydrogen in a new family, a number of members of which has already become known. Thus Deville has shown that on treating his toluol with sulphuric and nitric acids, the corresponding terms of hypo-sulphobenzolic acid, nitrobenzol, and dinitrobenzol are obtained. Investigations of the action of nitric acid on oil of anise by Cahours‡, and on Oleum dracunculi by Laurent§, have led to the discovery of anisylic, nitranisylic acids, and anisol (draconic, nitrodraconic acids and dracol), corresponding respectively to salicylic, nitrosalicylic acid and phenol; more recently Cahours‖ has found in hydride of anisyl even the term corresponding to hydride of salicyl, and Drs. Muspratt and Hofmann¶ have produced the organic base corresponding to aniline; in the paper in which this new and remarkable substance is described, these gentlemen have given a table, in which the analogy between the anisyl and salicyl groups has been pointed out.

In order to render this parallelism complete one principal term of the new series has hitherto been wanting, viz. the acid corresponding to benzoic acid. In the following paper will be pointed out the formation and properties of this substance, and the corresponding nitrogenous acid, both arising amongst the products of the oxidation of cymol.

* *Jahresbericht*, xxii. p. 354.

† On comparing the properties which Pelletier and Walter ascribe to retinaphtha with those of benzoène given by Deville, it is nearly certain that both substances are identical, though Deville seems to be inclined to establish a difference. A comparative study is however still wanting. Regarding dracyl, I may mention here that when engaged in the investigation of toluidin with Dr. Muspratt, we prepared a portion of this body according to the directions of Glenard and Boudault. The dracyl obtained possessed all the properties of toluol; we converted the body thus prepared into nitrodracyl (nitrotoluol), from which, by treatment with reducing agents, beautiful crystals of toluidin were obtained. In our paper on this organic base an analysis of the sulphate is given, and on referring I find that we forgot to mention that the salt analysed was prepared with the very toluidin obtained from the carbo-hydrogen arising with the distillation products of dragon's blood. This experiment removes any doubt that might have remained as to the identity of toluol and dracyl.—*Dr. A. W. Hofmann.*

‡ Liebig's *Annalen*, xli. 56. § Ibid. xliv. 313.

‖ Ibid. lvi. 307. ¶ Mem. of Chem. Soc. vol. ii. p. 367.

### *Preparation of Cymol.*

The experiments of Gerhardt and Cahours have shown that cumin oil (*oleum cumini*) is a mixture of two distinct oils,—cuminol ($C_{20}H_{12}O_2$), a body corresponding closely to oil of bitter almonds, and cymol ($C_{20}H_{14}$); by treatment with potash, the oxygen oil is converted into cuminic acid, while the carbo-hydrogen distils over unaltered. As, for the experiments about to be detailed, it was the latter of these two oils that was required, the mode of separation which I found it most convenient to adopt was the following:—The oil was first submitted to distillation alone, and about two-thirds of it drawn over; this portion was then repeatedly distilled with sticks of caustic potash, until the alkali remained unaltered; fresh potash was introduced after every third or fourth distillation, and the oil was regarded as pure when it ceased to lose anything after two or three distillations; latterly I found it advantageous to employ a retort of copper in this operation, the heated alkali proving exceedingly destructive to vessels of glass. The quantity of cymol obtained averaged about 7 oz. for every pound of cumin oil; and here I must be allowed to express my thanks to my friend Mr. Warington for having kindly undertaken to furnish me with a supply of oil obtained directly from the seeds by distillation: without his assistance I should scarcely have been able to have followed out my investigation, on account of the high price and varying quality of the oil obtained in commerce; from three-quarters of a hundred weight of seed Mr. Warington obtained at four distillations 2 lbs. 12 oz. of oil, which yielded me 18 oz. of beautiful and pure cymol.

To render cymol perfectly anhydrous, it was left for some time in contact with pieces of fused chloride of calcium and again distilled; in this state it is a limpid, colourless, highly refracting oil, of a very agreeable odour; its specific gravity I found to be 0·8576 at 16°, and its boiling-point, as a mean of two determinations with two specimens of the oil obtained at different periods, and which agreed closely with each other, 171°·5 C.

Cymol has been identified with camphogene, a substance previously obtained by Dumas*, by the action of anhydrous phosphoric acid on camphor, and lately studied by Delalande†. At the commencement of my experiments I thought that this might probably be a useful practical method of procuring the carbo-hydrogen; from the difficulty however of obtaining anhydrous phosphoric acid in sufficient quantities,

* Liebig's *Annalen*, vi. 249. † Ibid. xxxviii. 313.

and from the small amount of camphogene obtained, I found it otherwise, and I merely prepared a sufficient supply to enable me to obtain an additional proof of the identity of the two oils, which I did in a manner hereafter to be described. I may remark that even after repeated distillations with renewed quantities of anhydrous phosphoric acid I was unable to procure camphogene quite free from the peculiar smell of camphor, nor was there to be discovered in it the slightest approach to that fragrant odour by which cymol is characterized.

### *Action of Nitric Acid on Cymol.*

The action of nitric acid on cymol or camphogene has never hitherto been the subject of minute examination. Gerhardt and Cahours in their paper only mention that nitric acid of moderate concentration does not attack cymol when cold; that on heating nitrous acid is disengaged, and the carbohydrogen gradually passes into a peculiar acid, which on cooling is precipitated as a curdy mass; that this acid is rather soluble in water, alcohol and æther, crystallizing only with difficulty, and decomposed by heat, partially subliming in fine light needles or woolly flakes; and that fuming nitric acid decomposes cymol with the formation of the same acid and a yellow resin; none of these substances were however submitted by these chemists to elementary analysis. Delalande states that on treating camphogene with boiling fuming nitric acid it is converted into a white solid matter, becoming crystalline in the acid, and containing nitrogen. From these statements it seemed evident that the action of nitric acid on cymol gives rise to a variety of bodies, a supposition which experiments have completely verified; indeed, by a careful examination of this reaction, I have ascertained that not less than five or six different substances are produced; these bodies, some of which are acid, and some of a neutral character, are separated with considerable difficulty. In the present memoir I propose to confine myself to the acids only, reserving the regular substitution products of cymol, with the basic bodies arising therefrom, the substances representing nitrobenzol, aniline, &c., in the cymol series for a future paper.

I commenced with fuming nitric acid of the highest degree of concentration, the action of which on cymol is exceedingly violent; to avoid explosions it was necessary to keep the vessel cool by immersion in water; the oil was added gradually, drop by drop, to the acid, which speedily became of a dark red colour; by repeated distillations I obtained a beautiful crystalline acid, the analysis of which, leading to the formula

$HO, C_{16} H_6 NO_7$, rendered it evident, from the mode of its formation, that it must be considered as a substitution product of a corresponding non-nitrogenous acid, $HO, C_{16} H_7 O_3$, the very acid that is wanting in the toluol series, to the production of which acid my attention was now particularly directed.

Many attempts were made to oxidize the oil without having recourse to nitric acid; long-continued distillations with chromic acid, or with peroxide of manganese and sulphuric acid proved quite ineffectual, but after a great number of tentative operations, I at length succeeded, by the following method, in obtaining the wished-for substance, for which I propose the name of *toluylic acid*:—Ordinary nitric acid was diluted with about six times its bulk of water, and cymol added in the proportion of about 2 oz. of the oil to 1 lb. of the acid; the mixture was then introduced into a capacious retort and the distillation continued for two or three days; with acid of this strength there is no fear of a violent action; the oxidation of the oil proceeds slowly and quietly; it first becomes of a bright blue colour from the absorption of nitric oxide gas, then yellow, and after having been ten or a dozen times poured back into the retort, it begins to change more and more its physical character; it becomes heavier and more tenacious, and finally sinks to the bottom of the vessel; the process is known to be completed by a portion of the newly-formed acid passing over with the vapour of water, and condensing in the receiver, and if the whole operation has been successfully conducted, the contents of the retort become nearly solid on cooling from the crystallization of the acid; the weaker the nitric acid employed, and the longer the time consumed, the whiter and purer is the resulting acid; if a much stronger acid than that above prescribed be employed, violent action takes place when the boiling-point is reached, nearly the whole of the contents of the retort is projected into the receiver, and the new acid is found at the close of the operation to be contaminated with a considerable quantity of the nitrogenous acid, from which it is impossible afterwards entirely to free it; even when the operation has been slowly and carefully conducted with a very weak acid, it still contains a certain quantity of this acid, as numerous analyses proved, from which it is only to be freed by a series of troublesome operations; and it was only after a careful study and comparison of the salts formed by the respective acids that I was enabled to lay down a precise method for their separation. This method is founded on the great solubility of toluylate of baryta in cold water, and the very sparing solubility

of the corresponding salt of the nitrogenous acid in the same menstruum. The crude acid is thrown on a filter, and the adhering nitric acid removed by washing with cold water; it is then boiled with hydrate of lime, and the resulting lime-salt, filtered when quite cold, afterwards decomposed by nitric or hydrochloric acid; if the acid does not precipitate tolerably white, the same operation is repeated, and the well-washed acid is then dissolved in baryta water and carefully evaporated to dryness on the water-bath; it is redissolved in cold water, filtered, reprecipitated by hydrochloric acid, washed, and the process repeated until the dry baryta salt dissolves completely in cold water; it should then be once or twice crystallized, after which it is generally quite pure.

The quantity of pure acid as thus obtained from 2 oz. of cymol is very small, but I have not hitherto been fortunate enough to discover a better or less circuitous method of procuring it; could an oxidizing action be effected on the oil without the use of nitric acid a great saving would undoubtedly be achieved, but, as before stated, all my attempts in this direction proved unavailing; it is not impossible that the object may be obtained by permanganate of potash. I made one experiment with this salt, and there was evidently a reduction of the permanganic acid, but no trace of toluylic acid could be discovered, from which it seems evident that the oxidation had in this case proceeded too far and the cymol become converted into carbonic acid; this reaction has not however as yet been sufficiently studied.

### *Composition of Toluylic Acid.*

On submitting toluylic acid to elementary analysis in the usual manner, by burning it with oxide of copper, I obtained the following results:—

I. Acid obtained by sublimation, not having been previously treated with baryta:—0·2225 grm. gave 0·569 grm. carbonic acid and 0·1190 water.

II. Acid obtained as before from a new preparation:—0·2105 grm. gave 0·540 grm. carbonic acid and 0·1130 water.

III. Acid obtained from the lime salt:—0·160 grm. gave 0·415 grm. carbonic acid and 0·085 water.

IV. Acid obtained from the baryta salt:—0·3120 grm. gave 0·803 grm. carbonic acid and 0·161 water.

V. Acid obtained as before from a new preparation:—0·320 grm. gave 0·825 grm. carbonic acid and 0·1715 water.

These numbers correspond to the following per-centages:—

| | I. | II. | III. | IV. | V. |
|---|---|---|---|---|---|
| Carbon . | 69·74 | 69·96 | 70·09 | 70·19 | 70·31 |
| Hydrogen | 5·94 | 5·96 | 5·98 | 5·98 | 5·95 |

and with consideration of the atomic weight as deduced from the analysis of the silver and baryta salts, lead to the following formula, HO, $C_{16}$ $H_7$ $O_3$, as may be seen by the following comparison :—

| | | Theory. | | Mean of the three last experiments. |
|---|---|---|---|---|
| 16 equivs. | Carbon . . | 96 | 70·58 | 70·20 |
| 8 ... | Hydrogen . | 8 | 5·88 | 5·97 |
| 4 ... | Oxygen . . | 32 | 23·54 | |
| 1 ... | Toluylic acid | 136 | 100·00 | |

This acid thus becomes isomeric with hydride of anisyle and benzoate of oxide of methyl.

*Properties of Toluylic Acid.*

From an aqueous solution of any of its salts toluylic acid is precipitated by nitric or hydrochloric acid as a snow-white curdy mass, which under the microscope resolves itself into a great number of small acicular crystals: it is soluble to a considerable extent in boiling water, out of which it crystallizes on cooling in small needles; in alcohol, æther and pyroxylic spirit it is soluble almost to any extent; when heated it fuses and sublimes without decomposition in beautiful needles: in its state of perfect purity it is inodorous and tasteless, but the impure acid has a peculiar and sickening smell, somewhat resembling that of oil of bitter almonds. When boiled for some time with concentrated nitric acid, it loses an atom of hydrogen, in the place of which an atom of hyponitric acid enters, nitrotoluylic acid being formed; and when heated with caustic lime or baryta it is decomposed into carbonic acid and toluol.

In the formation of toluylic acid from cymol four equivalents of carbon and six equivalents of hydrogen are eliminated in the form of oxalic and carbonic acids and water. In several preparations large quantities of oxalic acid were found. There exists a striking similarity in the manner in which nitric acid acts upon cymol and oil of anise, an oil in its composition closely connected with cymol, and which gives rise to anisylic acid, between which and toluylic acid there is also a marked resemblance. The composition of oil of anise being $C_{20}$ $H_{12}$ $O_2$, we may consider it as cymol which has lost two equivalents of hydrogen and taken two of oxygen. The composition of the acids formed by the action of nitric acid on these two oils is as follows :—

Toluylic acid . . . . HO, $C_{16}$ $H_7$ $O_3$
Anisylic acid . . . . HO, $C_{16}$ $H_7$ $O_5$.

*Compounds of Toluylic Acid.*

From the extreme difficulty of obtaining this acid in a state of purity in any quantity, I have not been able to examine as many of its salts as I could have wished; the following will however serve to confirm its composition and establish its atomic weight.

*Toluylate of Baryta.*—The formation of this salt has been already described; I was unable to obtain it in a well-defined crystalline form. Its analysis yielded the following result:—

0·7955 grm. gave 0·453 sulphate of baryta = 37·37 per cent. baryta, agreeing very closely with the formula

$$BaO, C_{16} H_7 O_3,$$

as indicated by the subjoined comparison:—

| | | Theory. | Experiment. |
|---|---|---|---|
| 1 equiv. | Anhydrous acid | 127 | |
| 1 ... | Baryta . . . | 76 37·44 | 37·37 |

*Toluylate of Silver.*—This salt was formed by dropping nitrate of silver into a perfectly neutral solution of toluylate of ammonia; it fell as a white curdy mass, which was washed on a filter with cold water and purified by two or three crystallizations out of boiling water: it crystallizes in small needles. On analysing this salt the following numbers were obtained:—

I. 0·3785 grm. burned with oxide of copper gave 0·544 grm. of carbonic acid and 0·1045 water.

II. 0·334 grm. ignited gave 0·1485 silver.

III. 0·1725 grm. from another preparation gave 0·0767 silver.

IV. 0·1705 grm. from a third preparation gave 0·0757 silver.

These numbers correspond to the following per-centages:—

| | I. | II. | III. | IV. |
|---|---|---|---|---|
| Carbon . . | 39·198 | | | |
| Hydrogen . | 3·03 | | | |
| Silver . . . | | 44·46 | 44·46 | 44·4 |

and lead to the formula $AgO, C_{16} H_7 O_3$, as may be seen by the following comparison:—

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 16 equivs. | Carbon . . . . | 96 | 39·51 | 39·198 |
| 7 ... | Hydrogen . . . | 7 | 2·88 | 3·03 |
| 4 ... | Oxygen . . . | 32 | 13·17 | |
| 1 ... | Silver . . . . | 108 | 44·44 | 44·44 |
| 1 ... | Toluylate of silver | 243 | 100·00 | |

*Toluylate of Copper.*—This salt was prepared by dropping a solution of sulphate of copper into a perfectly neutral solution of toluylate of potash; it fell as a bright blue precipitate closely resembling the corresponding benzoate. It is very soluble in ammonia, forming a dark blue solution, and soluble to a slight extent in boiling water, separating on cooling as a granular precipitate: its analysis gave the following result.

0·3385 grm. ignited, the residue treated with nitric acid and again ignited gave 0·0822 grm. of oxide of copper = 24·28 per cent., agreeing with the formula $CuO, C_{16} H_7 O_3$.

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 1 equiv. | Anhydrous acid | 127·0 | 76·19 | |
| 1 ... | Oxide of copper | 39·7 | 23·81 | 24·28 |
| | | 166·7 | 100·00 | |

*Toluylate of Oxide of Ethyl.*—This compouud was formed by transmitting a stream of dry hydrochloric acid gas through a solution of the acid dissolved in strong alcohol, until the latter fumed strongly; it was then distilled, about two-thirds drawn over, and the residue in the retort mixed with water; the new æther precipitated in the form of a dark heavy liquid; it was digested with ammonia to remove any uncombined toluylic acid, well-washed with distilled water, dried, by being allowed to remain for some time in contact with pieces of fused chloride of calcium, and then distilled: it passed into the receiver nearly colourless, but on standing it deposited a small quantity of crystalline matter, which proved to be the æther of the nitrogenous acid, the acid employed not having been obtained from the baryta salt. By a second distillation, collecting only the first portions, the whole of the other æther was removed and a pure substance obtained.

*Analysis.*—0·223 grm. gave 0·596 carbonic acid and 0·151 water. Centesimally,—

| | |
|---|---|
| Carbon . . . . . | 72·9 |
| Hydrogen . . . . | 7·52 |

agreeing closely with the formula $C_4 H_5 O, C_{16} H_7 O_3$, as the following comparison of the theoretical with the experimental numbers shows:—

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 20 equivs. | Carbon . . . | 120 | 73·17 | 72·90 |
| 12 ... | Hydrogen . . | 12 | 7·31 | 7·52 |
| 4 ... | Oxygen . . . | 32 | 19·52 | |
| 1 ... | Toluylic æther . | 164 | 100·00 | |

When perfectly pure this compound is a colourless, fra-

grant liquid, having an odour closely resembling that of cinnamic or benzoic æther, and a pungent and slightly bitter taste. It boils at 228° C., which temperature may perhaps be one or two degrees too high, the determination having been made before the last traces of the nitrogenous æther had been removed; still it exhibits a new confirmation of the observation of H. Kopp, that the difference in the boiling-points of two analogous compounds, which differ by two equivalents of carbon and two of hydrogen, is 19° C. Benzoic æther, the composition of which is $C_4 H_5 O$, $C_{14} H_5 O$, boils at 209°. Unfortunately I had not a sufficient quantity of the liquid after purification for a second determination.

The following salts I have examined qualitatively only, considering the composition and atomic weight of the acid well-enough established by the preceding analyses.

*Toluylate of Potash*, formed by exactly neutralizing the acid with caustic potash, is a very soluble salt, crystallizing with great difficulty in small needles.

*Toluylate of Soda* is still more soluble than the preceding. I could not obtain it in the crystalline state.

*Toluylate of Ammonia* crystallizes in small prisms.

*Toluylate of Lime* crystallizes out of a concentrated aqueous solution in long shining needles.

### *Products of the Decomposition of Toluylic Acid.*

*Nitrotoluylic Acid.*—I have already observed that on treating cymol with concentrated and fuming nitric acid violent action ensues, and that by repeated distillations a crystalline acid containing nitrogen is obtained. I must now describe this action more in detail. The nitric acid employed should be concentrated and fuming, otherwise there will be a considerable formation of another crystalline substance, which is in its chemical character neutral, and which is not easily converted into nitrotoluylic acid. The properties and composition of this new product will be fully considered hereafter. The distillation must be continued as long as nitrous fumes continue to be evolved, and the retort then allowed to cool, upon which a considerable quantity of crystalline matter is deposited, and on adding cold water a copious precipitate takes place. The whole is now thrown on a filter and washed with cold water till all the nitric acid is removed; the precipitate is then digested with ammonia, the greater part dissolves; a portion however collects at the bottom of the vessel in the form of a red oil, which is to be separated. The ammoniacal salt is next decomposed by hydrochloric acid, the acid collected on a filter and well-washed with cold water, in

which it is very sparingly soluble; it is then dissolved in hot alcohol, boiled for a few minutes with animal charcoal, and filtered; by spontaneous evaporation the new acid crystallizes out in beautiful rhombic prisms of a pale yellow colour.

*Composition of Nitrotoluylic Acid.*

The powdered crystals by combustion with oxide of copper yielded the following numbers:—

I. 0·330 grm. gave 0·640 carbonic acid and 0·1205 water.

II. 0·382 grm. gave 0·7396 carbonic acid and 0·136 water.

III. 0·4145 grm. gave 0·806 carbonic acid and 0·152 water.

IV. The nitrogen was determined by Dumas' method in an atmosphere of carbonic acid. The particulars of the experiment are as follows:—

0·600 grm. gave 41·5 cubic cent. of moist nitrogen. Barometer $0^{m}\cdot7973$; Thermometer $18^{\circ}\cdot5$ C.

These numerical results correspond with the following per cents.:—

| | I. | II. | III. | IV. |
|---|---|---|---|---|
| Carbon . . | 52·89 | 52·80 | 53·03 | |
| Hydrogen . | 4·06 | 3·95 | 4·07 | |
| Nitrogen . . | ... | ... | ... | 79·6 |

and lead to the formula HO, $C_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_3$, as the following comparison of the calculated numbers with the mean of analysis shows:—

| | | Theory. | | Mean of expt. |
|---|---|---|---|---|
| 16 eqs. | Carbon . . . . | 96 | 53·03 | 52·90 |
| 7 ... | Hydrogen . . . | 7 | 3·86 | 4·00 |
| 1 ... | Nitrogen . . . | 14 | 7·74 | 7·96 |
| 8 ... | Oxygen . . . . | 64 | 35·37 | |
| 1 ... | Nitrotoluylic acid | 181 | 100·00 | |

By the following analyses of some of the salts of this acid the above formula is fully confirmed, and the atomic weight of the acid proved.

*Nitrotoluylate of Baryta.*—This salt was formed by adding chloride of barium to a neutral solution of nitrotoluylate of ammonia. A white curdy precipitate was determined, soluble to a considerable extent in boiling water, out of which it crystallized on cooling in beautiful stellated tufts, having a shining appearance when dry: after two or three recrystallizations it was submitted to analysis, and yielded the following results:—

0·738 grm. gave by ignition 0·290 grm. of carbonate of

baryta = 30·54 per cent. baryta, corresponding with the formula $BaO, C_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_3$, as may be seen by the following comparison :—

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 1 equiv. | Anhydrous acid | 171·50 | 69·24 | |
| 1 ... | Baryta . . . | 76·66 | 30·76 | 30·54 |
| | | 248·16 | 100·00 | |

*Nitrotoluylate of Silver.*—This salt was formed by dropping nitrate of silver into a neutral solution of nitrotoluylate of ammonia; it fell as a white curdy mass resembling chloride of silver. It is soluble to a considerable extent in hot water, and by long boiling becomes partially decomposed; it crystallizes from a hot aqueous solution in beautiful feathery tufts; it is only sparingly soluble in alcohol.

By combustion with oxide of copper the following results were obtained :—

I. 0·3505 grm. gave 0·424 grm. carbonic acid and 0·070 water when ignited alone.

II. 0·3385 grm. gave 0·127 grm. of silver.

III. 0·230 grm. gave 0·086 grm. silver. Centesimally :—

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . | 33·0 | | |
| Hydrogen . | 2·12 | | |
| Silver . . . | ... | 37·52 | 37·38 |

corresponding with the formula $AgO, C_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_3$.

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 16 equivs. | Carbon . . | 96 | 33·33 | 33·00 |
| 6 ... | Hydrogen . | 6 | 20·8 | 2·12 |
| 1 ... | Nitrogen . . | 14 | 4·86 | |
| 8 ... | Oxygen . . | 64 | 22·22 | |
| 1 ... | Silver . . . | 108 | 37·51 | 37·45 |
| 1 ... | Nitrotoluylate of silver . | 288 | 100·00 | |

I have already mentioned that I prepared a small quantity of camphogene by the action of anhydrous phosphoric acid on camphor; in order to obtain an additional experimental proof of the identity of this substance with cymol, I have studied the action of concentrated nitric acid on it. I found it most convenient to prepare a silver salt of the acid thus obtained, the analysis of which yielded me the following numbers :—

I. 0·396 grm. gave 0·486 carbonic acid and 0·85 water.
II. 0·372 grm. gave 0·139 silver.
III. 0·2935 grm. gave 0·110 silver.
These numbers correspond in per cents. to—

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . . | 33·46 | | |
| Hydrogen . . | 2·38 | | |
| Silver . . . . | ... | 37·36 | 37·47 |

And by comparing them with the preceding they will be found sufficiently near to warrant the conclusion that the two carbo-hydrogens are identical. On treating the acid formed by the action of fuming nitric acid on camphogene with ammonia, the same heavy oil which was observed in the case of cymol separated, and after a while crystallized; but from the small quantity of camphogene at my command, I was unable to procure sufficient of this substance for a comparative experiment, or to bring forward any additional proof of the identity of the two oils.

*Nitrotoluylate of Lime.*—This salt was prepared by decomposing nitrotoluylate of ammonia by chloride of calcium. It fell as a granular crystalline mass, much more soluble in water than the corresponding baryta salt, and crystallizing out of its aqueous solution in small clustering groups of oblique rhombic prisms; it was obtained perfectly pure by two or three recrystallizations.

*Analysis.*—0·6965 grm. gave by ignition, treatment with carbonate of ammonia, and a second gentle ignition, 0·1775 grm. carbonate of lime = 14·27 per cent. of lime, agreeing exactly with the formula $Ca, OC_{16}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right\}O_3$.

| | Theory. | Experiment. |
|---|---|---|
| 1 equiv. Anhydrous acid | 171·50 | |
| 1 ... Lime . . . . | 28·5 | 14·25 | 14·27 |
| | 200·00 | |

*Nitrotoluylate of Oxide of Ethyl.*—A solution of the pure acid in strong alcohol was submitted to a current of dry hydrochloric acid gas till copious fumes were evolved; it was then distilled; the first portions that passed into the receiver consisted of a mixture of alcohol and hydrochloric æther; the distillation was continued until a few drops collected on a watch-glass gave a milkiness when mixed with water; it was then stopped, and the retort allowed to cool; a considerable quantity of the yellow heavy oil collected at the bottom of the vessel, which was poured off into a beaker; in a few

minutes it solidified into a yellow crystalline mass. This impure æther was next treated with carbonate of potash, by which all adhering undecomposed acid was removed; it was then thrown on a filter, well-washed with cold water, and dried by pressure between folds of bibulous paper; it was now of a pale amber colour, and possessed a very agreeable odour; it was redissolved in hot alcohol and filtered, the alcoholic solution on cooling solidified into a light lemon-coloured crystalline mass; this was dried between folds of blotting-paper, transferred to a watch-glass, and, placed in the water-bath, it immediately liquefied: after remaining about an hour it was removed, and on cooling it gradually crystallized into a mass of needles radiating from a common centre and having a very beautiful appearance.

It was analysed by combustion with oxide of copper, and furnished the following results:—

0·362 grm. gave 0·760 grm. carbonic acid and 0·175 grm. water. Centesimally—

| | |
|---|---|
| Carbon . . . . | 57·26 |
| Hydrogen . . . | 5·37 |

agreeing with the formula $C_4 H_5 O, C_{16}\left\{\begin{matrix} H_6 \\ NO_4 \end{matrix}\right\} O_3$, as shown by the following comparison:—

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 20 eqs. | Carbon . . . . . | 120 | 57·42 | 57·26 |
| 11 ... | Hydrogen . . . . . | 11 | 5·26 | 5·37 |
| 1 ... | Nitrogen . . . . . | 14 | 6·69 | |
| 8 ... | Oxygen . . . . . | 64 | 30·63 | |
| 1 ... | Nitrotoluylic æther . | 209 | 100·00 | |

The remainder of the æther was dissolved in a strong alcoholic solution of ammonia and set aside with the view of procuring nitrotoluylamide: this substance, however, which it would have been interesting to have compared with the corresponding term of the benzoyl series lately obtained by Mr. Field*, I have not yet been able to obtain.

*Nitrotoluylate of Oxide of Methyl.*—To prepare this substance, nitrotoluylic acid was dissolved in pure pyroxylic spirit, and the solution subjected to a long-continued stream of dry hydrochloric acid gas, as in the corresponding ethyl compound. On distilling the fuming acid liquid, a considerable quantity of a dense, black oily substance collected at the bottom of the vessel: this was evidently the methyl compound contaminated with results of the decomposition of the

* Memoirs of the Chemical Society, vol. iii. p. 404.

pyroxylic spirit by the hydrochloric acid gas. On cooling the acid liquid was poured off and the oil repeatedly washed with water; in a few hours it solidified into a confused crystalline mass, still however black and having a peculiar vinous smell: an attempt was made to purify it by distillation with water; in consequence, however, of its high boiling-point, very little passed over into the receiver after two or three hours' distillation. It was then heated with strong nitric acid, and after boiling for a few minutes, water added; the æther now readily separated in clear, light yellow oily drops: ammonia was then added to remove any nitrotoluylic acid that might have been present, and the oil collected on a watch-glass; in a few minutes it solidified into a crystalline mass, which was dissolved in æther, filtered and recrystallized, and then exposed for some time to the heat of the water-bath; on cooling it solidified as before, and was then considered sufficiently pure for analysis.

0·376 grm. gave by combustion with oxide of copper 0·756 grm. of carbonic acid and 0·164 grm. of water, corresponding in per cents. to

| | |
|---|---|
| Carbon . . . . | 54·84 |
| Hydrogen . . . | 4·83 |

and agreeing with the formula $C_2 H_3 O, C_{16} \left\{ \begin{matrix} H_6 \\ NO_4 \end{matrix} \right\} O_3$.

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 18 eqs. | Carbon . . . . | 108 | 55·38 | 54·84 |
| 9 ... | Hydrogen . . . | 9 | 4·61 | 4·83 |
| 1 ... | Nitrogen . . . | 14 | 7·18 | |
| 8 ... | Oxygen . . . . | 64 | 32·83 | |
| 1 ... | Nitrotoluylate of oxide of methyl . . | 195 | 100·00 | |

After standing two or three days, beautiful colourless stellar crystals were deposited on the sides of the vessel containing an aqueous solution of this æther; it is probable, therefore, that this as well as the last-described compound is, when perfectly pure, colourless. The two æthers closely resemble each other in their physical characters, the smell of the latter is, however, less agreeable than that of the former; both are decomposed by potash into nitrotoluylic acid and alcohol or pyroxylic spirit.

The following salts of this acid I merely examined qualitatively.

*Nitrotoluylate of Potash* is a very soluble salt crystallizing with great difficulty in small needles.

*Nitrotoluylate of Soda*, like the corresponding salt of toluylic acid, I could not obtain in any definite crystalline form.

*Nitrotoluylate of Ammonia* crystallizes out of its aqueous solution in long needles; it is very easily decomposed, losing the whole of its ammonia when boiled with animal charcoal. I intend to return to the study of this salt, and hope to obtain from it the body which I failed to procure from nitrotoluylic æther, viz. nitrotoluylamide.

*Nitrotoluylate of Strontia.*—This salt, which in appearance is not to be distinguished from the corresponding baryta salt, was formed by dropping chloride of strontium into neutral nitrotoluylate of ammonia: it is rather more soluble in boiling water than the baryta compound, and the crystals deposited on cooling are rather larger.

*Nitrotoluylate of Copper.*—On adding solution of sulphate of copper to perfectly neutral nitrotoluylate of ammonia a basic salt is formed. I have not yet obtained a definite copper salt of this acid.

*Action of a mixture of Sulphuric and Nitric Acids on Nitrotoluylic Acid.*

When nitrobenzol is boiled repeatedly with the strongest nitric acid it loses an atom of hydrogen, in the place of which another atom of hyponitric acid enters. The transformation proceeds very slowly. The new substance (dinitrobenzol) is however obtained very speedily, as Drs. Muspratt and Hofmann* have shown, by dropping benzol or nitrobenzol into a mixture composed of equal parts of fuming nitric acid and concentrated sulphuric acid as long as the liquid remains homogeneous. This method has lately been employed with great success by M. Cahours, who, amongst many other interesting products, has obtained trinitranisic acid, $C_{16}\left\{\begin{matrix}H_5\\3(NO_4)\end{matrix}\right\}O_6$; dinitrocuminic acid, $C_{20}\left\{\begin{matrix}H_{10}\\2(NO_4)\end{matrix}\right\}O_4$; and dinitrobenzoic acid, $C_{14}\left\{\begin{matrix}H_4\\2NO_4\end{matrix}\right\}O_4$. It appeared interesting to submit nitrotoluylic acid to a similar treatment, but after digesting the acid with the mixture for several days the anticipated transformation had not taken place, the numbers obtained by analysis being those given under III., "composition of nitrotoluylic acid." I intend however to repeat this experiment.

*Distillation of Toluylic Acid with Baryta—Toluol.*

Although the preceding analyses of toluylic and nitroto-

* Mem. Chem. Soc. vol. iii. p. 111.

luylic acids have established the composition of these two compounds in a perfectly satisfactory manner, there still remained one experiment to be made in order to prove that toluylic acid occupies in the toluyl series the same place which benzoic acid has in the benzoyl series; in order to prove that the acids analysed are really the true toluylic and nitrotoluylic acids, and not merely bodies having the same composition, being isomeric with them: this experiment was to attempt the transformation of toluylic acid into toluol under the same circumstances by which benzoic acid becomes converted into benzol. I devoted the acid from four ounces of cymol to this experiment, and by distillation with caustic baryta, which I found to answer much better than lime, I obtained some grammes of a beautiful limpid colourless liquid, having the precise smell of the carbo-hydrogen sought for. By distillation from a fresh portion of baryta the oil was rendered perfectly anhydrous; in this state its boiling-point was taken. It began to boil at 109°, the thermometer gradually rose to 110°·5, barometer $0^{m}{\cdot}763$ (30·1 inches).

It was burned in the ordinary manner with oxide of copper and yielded the following results:—

0·2410 grm. gave 0·809 grm. of carbonic acid and 0·196 grm. of water, corresponding in per cents. to

| | |
|---|---|
| Carbon . . . . | 91·50 |
| Hydrogen . . . | 9·03 |

and agreeing exactly with the formula of toluol, $C_{14}H_8$, as the following comparison shows:—

| | Theory. | | Experiment. |
|---|---|---|---|
| 14 eqs. Carbon . . . | 84 | 91·3 | 91·50 |
| 8 ... Hydrogen . . | 8 | 8·7 | 9·03 |
| | 22 | 100·0 | 100·53 |

The formation of toluol from toluylic acid is perfectly analogous to the production of benzol from benzoic acid.

$$\underbrace{C_{16}H_8O_4}_{\text{Toluylic acid.}} + 2BaO = \underbrace{C_{14}H_8}_{\text{Toluol.}} + 2(BaO, CO_2).$$

The remainder of the carbo-hydrogen was converted into nitrotoluol by the action of fuming nitric acid: the well-washed oily fluid was then dissolved in alcohol, saturated with ammoniacal gas and treated repeatedly with sulphuretted hydrogen, the whole being distilled after each saturation with hydrosulphuric acid, to facilitate the deposition of the sulphur; the dark red solution was evaporated to expel the alcohol, water added, and then submitted to distillation with

potash, in addition to ammonia and aqueous vapour, a yellow oil passed into the receiver, which did not however solidify on cooling, probably in consequence of the presence of ammonia; it was therefore saturated with oxalic acid, evaporated to dryness in the water-bath, redissolved in boiling alcohol and filtered; on cooling, oxalate of toluidine separated in fine white needles, these were washed, dissolved in boiling water, and decomposed by potash; the toluidine, which separated in colourless oily drops, was taken up by æther, on the evaporation of which it remained in the form of a crystalline mass. Although the nature of this substance was sufficiently obvious, nevertheless, to remove all doubt respecting it, I converted it into the double platinum salt by mixing it with hydrochloric acid and bichloride of platinum. The beautiful orange-yellow spangular mass was washed with æther and dried on the water-bath. Its analysis gave the following result:—

0·930 grm. gave by ignition 0·292 grm. of platinum = 31·398 per cent.

This determination agrees with the formula for chloride of platinum and toluidine—$C_{14}\,H_9\,N$, H Cl, $PtCl_2$.

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| 14 eqs. | Carbon . . . | 84·00 | | |
| 9 ... | Hydrogen . . | 9·00 | | |
| 1 ... | Nitrogen . . | 14·00 | | |
| 3 ... | Chlorine . . | 106·50 | | |
| 1 ... | Platinum . . | 98·68 | 31·6 | 31·398 |
| | | 312·18 | | |

By the production of toluylic and nitrotoluylic acids there is not only filled up a gap which has hitherto existed in the toluyl series, but an important step has been made in the series of acids to which I have alluded at the commencement of this paper, of which indeed at the present time a few scattered members only are known. The following table presents a general view of some of the most important members of the different groups, and exhibits the gaps which remain to be filled up by future experiments.

| I. | II. | III. | IV. | V. | VI. |
|---|---|---|---|---|---|
| $HO, C_{12}H_3O_5$ unknown | Salicylic acid..... $HO, C_{14}H_5O_5$ | Anisylic acid ..... $HO, C_{16}H_7O_5$ | $NO, C_{18}H_9O_5$ unknown. | $HO, C_{20}H_{11}O_5$ unknown. | $HO, C_{22}H_{13}O_5$ unknown |
| | Nitrosalicylic acid... $HO, C_{14}\{H_4, NO_4\}O_5$ | Nitranisylic acid.. $HO, C_{16}\{H_6, NO_4\}O_5$ | | | |
| | Phenol ..... $HO, C_{12}H_5O$ | Anisol ..... $HO, C_{14}H_7O$ | | | |
| | Oil of bitter almonds $H, C_{14}H_5O_2$ | ..... | ..... | Hydride of Cuminyl, $H, C_{20}H_{10}O_2$ | |
| | Benzoic acid..... $HO, C_{14}H_5O_3$ | Toluylic acid..... $HO, C_{16}H_7O_3$ | ..... | Cuminic acid..... $HO, C_{20}H_{11}O_3$ | |
| | Nitrobenzoic acid... $HO, C_{14}\{H_4, NO_4\}O_3$ | Nitrotoluylic acid, $HO, C_{16}\{H_6, NO_4\}O_3$ | ..... | Nitrocuminic acid, $HO, C_{20}\{H_{10}, NO_4\}O_3$ | |
| | Dinitrobenzoic acid, $HO, C_{14}\{H_3, 2NO_4\}O_3$ | ..... | ..... | Dinitrocuminic acid ..... $HO, C_{20}\{H_9, 2NO_4\}O_3$ | |
| | Benzonitrile ..... $C_{14}H_5N$ | ..... | ..... | Cumonitrile ..... $C_{20}H_{11}N$ | |
| | Benzol ..... $C_{12}H_6$ | Toluol ..... $C_{14}H_8$ | ..... | Cumol..... $C_{18}H_{12}$ | Cymol, $C_{20}H_{14}$ |
| | Nitrobenzol ..... $C_{12}\{H_5, NO_4\}$ | Nitrotoluol ..... $C_{14}\{H_7, NO_4\}$ | ..... | Nitrocumol..... $C_{18}\{H_{11}, NO_4\}$ | |
| | Dinitrobenzol ..... $C_{12}\{H_4, 2NO_4\}$ | Dinitrotoluol..... $C_{14}\{H_6, 2NO_4\}$ | ..... | Dinitrocumol ..... $C_{18}\{H_{10}, 2NO_4\}$ | |
| Seminaphthalidine $C_{10}H_5N$ | Aniline ..... $C_{12}H_7N$ | Toluidine ..... $C_{14}H_9N$ | ..... | Cumidine ..... $C_{18}H_{13}N$ * | |
| | Nitraniline..... $C_{12}\{H_6, NO_4\}N$ | | | | |
| | Bromaniline ..... $C_{12}\{H_6, Br\}N$ | | | | |
| | Dibromaniline ..... $C_{12}\{H_4, Br_2\}N$ | | | | |
| | Tribromaniline ..... $C_{12}\{H_6, Br_3\}N$ | | | | |

* This beautiful base has lately been prepared by Mr. Nicholson in the laboratory of the Royal College of Chemistry.

The preceding table shows that there are indeed a great number of substances still to be discovered. In the first series it will be seen that as yet we have only one member, seminaphthalidine*, the base corresponding to aniline and toluidine, and obtained by Zinin in a very curious reaction of sulphide of ammonium on dinitronaphthalol. The second series is best known; it is closely connected with the indigo series by salicylic acid, nitrosalicylic acid and aniline. As however the term of indigo is as yet not represented in any of the other families I have omitted to connect them. The third is the toluyl series, which has become enriched by the present investigation with two of the principal terms: of the following no term whatever is known. The next contains a series of interesting compounds arising from oil of cumin, and of the last group we have at present only cymol. In a future paper I hope to introduce some of the substances deriving from this carbo-hydrogen.

This investigation was conducted in the laboratory of the Royal College of Chemistry, and I cannot bring it to a conclusion without acknowledging the great obligation I am under to Professor Hofmann for the constant advice and assistance which he afforded me during its prosecution, and expressing my warmest thanks to him for his valuable instructions in the method of conducting organic investigations generally.

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June 21, 1847.—The President in the Chair.

Four Numbers of Silliman's Journal were presented by the Editor.

The following papers were read:—

A notice from Messrs. Playfair and Joule on the next part of their paper on Atomic Volume.

## CCIII. *On some of the Products of Oxidation of Cumol by Nitric Acid.* *By* Mr. F. A. Abel.

FROM the investigations on the action of nitric acid upon organic bodies, *one* result, in reference to the manner in which this acid acts, has been undoubtedly established. We know that in most cases the carbon of the organic substance remains untouched; that according to the degree of concentration of the acid a smaller or larger number of equivalents of hydrogen are expelled, and that the remaining part of the organic body combines with the remainder of the nitric acid. Thus is produced that innumerable class of neutral com-

* Erdmann's Journal, xxxiii. 29.

pounds considered by some chemists to be combinations of nitrous acid with organic oxides, and by others to be products of the substitution of hyponitric acid for hydrogen. It is indifferent which of these views is adopted, the fact having been established by hundreds of experiments, and we are enabled by analogy to predict with tolerable certainty the result of any new experiment.

The case is quite different when the oxidation is not confined to the hydrogen, but is extended to the carbon. The numerous experiments made on this subject do not as yet afford any general conclusion; we are far from being able to form an opinion, previous to experiment, of the nature of the product formed. This will be obvious if we examine the action of nitric acid on a class of bodies which are very nearly related to each other, both by the manner in which they are formed and in their general chemical behaviour. Benzol, toluol, cinnamol (styrol), cumol, naphthalol, cymol, are acted upon by nitric acid, the corresponding products of substitution are formed.

| | | | | | |
|---|---|---|---|---|---|
| Benzol | $C_{12}H_6$ | Nitrobenzol | $C_{12}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right\}$ | Dinitrobenzol | $C_{12}\left\{\begin{matrix}H_4\\2NO_4\end{matrix}\right\}$ |
| Toluol | $C_{14}H_8$ | Nitrotoluol | $C_{14}\left\{\begin{matrix}H_7\\NO_4\end{matrix}\right\}$ | Dinitrotoluol | $C_{14}\left\{\begin{matrix}H_6\\2NO_4\end{matrix}\right\}$ |
| Cinnamol | $C_{16}H_8$ | Nitrocinnamol | $C_{16}\left\{\begin{matrix}H_7\\NO_4\end{matrix}\right\}$ | | |
| Cumol | $C_{18}H_{12}$ | Nitrocumol | $C_{18}\left\{\begin{matrix}H_{11}\\NO_4\end{matrix}\right\}$ | Dinitrocumol | $C_{18}\left\{\begin{matrix}H_{10}\\2NO_4\end{matrix}\right\}$ |
| Naphthalol | $C_{20}H_8$ | Nitronaphthalol | $C_{20}\left\{\begin{matrix}H_7\\NO_4\end{matrix}\right\}$ | Dinitronaphthalol | $C_{20}\left\{\begin{matrix}H_6\\2NO_4\end{matrix}\right\}$ |
| Cymol | $C_{20}H_{14}$ | Nitrocymol | $C_{20}\left\{\begin{matrix}H_{13}\\NO_4\end{matrix}\right\}$* | | |

In the above two columns of combinations the number of equivalents of carbon will be found the same as in the carbo-hydrogens. We have however succeeded with most of these bodies, by the continued action of the acid upon them, or by the observation of particular conditions, in oxidizing also a portion of their carbon bodies with acid properties being produced which contain a smaller number of equivalents of carbon than the carbo-hydrogens from which they were derived. The composition of these acids does not however bear any constant relation to the carbo-hydrogens, such as observed in the above-mentioned products of substitution.

By the continued action of nitric acid on naphthalol, naphthalic acid, discovered by Laurent and Marignac†, is produced, the composition of which is expressed by the formula

$$2HO, C_{16}H_4O_6.$$

* This substance is now under investigation by Mr. Noad.—Dr. A. W. H.

† Liebig's *Annalen*, xli. p. 98, and xlii. p. 215.

The action of nitric acid on cinnamol (styrol) has been studied by Drs. Hofmann and Blyth*. They have shown that cinnamol may in this manner be converted into benzoic acid.

The products obtained by the action of nitric acid on toluol have been studied by Deville†. He found that the two above-mentioned products of substitution were easily formed. He moreover believes to have converted toluol, by a long treatment with oxidizing agents, into benzoic acid; he is however in doubt about the result of his experiment, as he could not always succeed in the transformation, and his method of preparing toluol did not exclude the possibility of its containing benzoic æther in admixture. If benzoic acid can in reality be obtained from toluol, we have here an instance of the formation of an acid without the original number of equivalents of carbon in the carbo-hydrogen being diminished.

In the paper lately read before this Society by Mr. Noad, he has shown that cymol is converted by the continued action of dilute nitric acid into toluylic acid.

It will be seen from these examples that we are unable to determine anything beforehand regarding the nature of these products of oxidation. The manner in which nitric acid or any other oxidizing agent acts is evidently closely connected with the constitution of the body exposed to their influence. Aided by the manner in which nitric acid acts on naphthalol, Marignac has in fact founded a view of the constitution of this body. He considers the carbo-hydrogen in question to be a combination of two others, namely, $C_{16}H_4$ and $C_4H_4 = C_{20}H_8$, naphthalic acid, $C_{16}H_4O_6$, being formed by the action of nitric acid on the first, while the other is converted by the influence of the oxygen into water and oxalic acid or carbonic acid. By this view many of the reactions of naphthalol may be explained in a very satisfactory manner. It is possible that similar views may be applied to the other carbo-hydrogens, by which their behaviour with oxidizing agents may be similarly explained; a great number of investigations are however required before we can arrive at any general result.

The following experiments, which I have instituted at the suggestion and under the direction of Dr. Hofmann, may, I hope, be considered as a slight contribution to this subject.

It is known that when cumol is treated with concentrated nitric acid it yields the usual products of substitution of the carbo-hydrogens. Gerhardt and Cahours have observed further, that by the continuous action of dilute nitric acid on

* Trans. of Chem. Soc. vol. ii. p. 334.

† *Ann. de Chim. et de Phys.* 3d Ser. t. iii. p. 168.

cumol a crystalline acid is produced*. This acid has not, however, been more closely investigated. According to the experiments on toluol, cinnamol and cymol before mentioned, this acid might be of three different kinds, according to the analogy of cumol with any one of these carbo-hydrogens. If the number of equivalents of carbon were to remain the same as in toluol, the acid obtained might be HO, $C_{18} H_9 O_3$, until now unknown (differing from toluylic or cuminic acid in containing $C_2 H_2$, more or less). Should two equivalents of carbon be eliminated, as is the case with cinnamol, the formation of toluylic acid might then be expected; and lastly, should cumol be analogous to cymol, that is, should it lose four equivalents of carbon, the acid must then be benzoic acid.

In the preparation of cumol I proceeded in the manner described by its discoverers, Gerhardt and Cahours. Pure cuminic acid was distilled with four times its weight of caustic lime in a copper retort placed in a deep sand-bath, the temperature of which was gradually raised to a red heat. The distillate obtained was colourless, possessing however an empyreumatic odour, which it did not lose on being rectified over hydrate of potash to free it from any cuminic acid that might have come over with it. I afterwards found that this peculiar odour was immediately removed on distilling the oil with a concentrated solution of chromic acid, which leaves the cumol of its agreeable aromatic smell without affecting its composition. This is a method that might perhaps prove useful in many cases where the peculiar odour of a carbo-hydrogen is disguised by the presence of a small quantity of some foreign substance.

When dried over chloride of calcium this body possessed exactly the same properties as described by Gerhardt and Cahours. Its boiling-point was found by them to be 144° C.; a later experiment of Gerhardt gave 153° as the boiling-point. The cumol that I prepared boiled at 148° C. Its analysis gave me the following results:—

0·2029 grm. burned with oxide of copper gave 0·6725 grm. of carbonic acid and 0·1804 grm. of water; corresponding to

| | |
|---|---|
| Carbon . . . . | 90·34 |
| Hydrogen . . . | 9·88 |

which numbers agree with the composition of cumol.

| | | Theory. | Found. |
|---|---|---|---|
| 18 eqs. Carbon . . | 108 | 90·0 | 90·34 |
| 12 ... Hydrogen . | 12 | 10·0 | 9·88 |
| | 120 | 100·0 | |

* Liebig's *Annalen*, xxxviii. p. 67.

On boiling cumol with concentrated nitric acid it is quickly converted into a heavy oil, which is the analogue to nitrobenzol. If the boiling is continued this oil disappears, and is gradually converted into a yellow crystalline mass, soluble in ammonia with the exception of a slight fixed residue (dinitrocumol). The ammoniacal solution gives with hydrochloric acid a white precipitate, difficultly soluble in cold water, but more easily so in hot water, from which it crystallizes on cooling. These crystals are generally somewhat coloured; recrystallization after treatment with animal charcoal removes this colouring matter.

Several combustions of the acid dried at 100° C. showed me that my substance must be a mixture. I therefore distilled another portion of cumol with fuming nitric acid for several days, and obtained a crystalline body similar to the former, which was purified in the usual manner. A combustion of this body gave me the following results:—

0·2628 grm. of substance yielded 0·4890 grm. carbonic acid and 0·0743 grm. water.

Or in 100 parts,—

| | |
|---|---|
| Carbon . . . . | 50·73 |
| Hydrogen . . . | 3·18 |

These numbers correspond to the composition of nitrobenzoic acid, $HO, C_{14}\left\{\begin{matrix}H_4\\NO_4\end{matrix}\right\}O_3$, as is seen when compared with the theoretical numbers.

| | | | Theory. | Found. |
|---|---|---|---|---|
| 14 equivs. | Carbon . . | 84 | 50·30 | 50·73 |
| 5 ... | Hydrogen . | 5 | 3·00 | 3·18 |
| 1 ... | Nitrogen . . | 14 | 8·38 | |
| 8 ... | Oxygen . . | 64 | 38·32 | |
| | | 167 | 100·00 | |

On addition of nitrate of silver to the ammoniacal salt of this acid a white precipitate was formed, sparingly soluble in hot water, from which it crystallized on cooling. I had not sufficient substance to recrystallize the salt, and could therefore only purify it by washing.

Its analysis gave me the following result:—

0·1657 grm. of substance left, on being burnt, 0·0650 grm., or 39·24 per cent. of silver; which agrees sufficiently well with the composition of nitrobenzoate of silver.

| | | Theory. | Found. |
|---|---|---|---|
| Nitrobenzoic acid . | 158 | 57·67 | |
| Oxide of silver . . | 116 | 42·33 | 42·14 |
| | 274 | 100·00 | |

In order to be perfectly certain, the small quantity remaining of the silver salt was submitted to distillation. There sublimed a portion of the acid, mixed with a few drops of an aromatic oil. The product of the distillation was therefore submitted to Dr. Hofmann's process for detecting nitrobenzol; it was dissolved in a mixture of alcohol and sulphuric acid, and reduced by means of a piece of metallic zinc. After the disengagement of hydrogen had ceased, the liquid was neutralized with potash and agitated with æther. A few drops of the ætherial solution gave, on evaporation with hypochloride of lime, the beautiful violet colour characterizing aniline.

These experiments were sufficient to identify nitrobenzoic acid, and it seemed more than probable that the excess of carbonic acid obtained in the first analysis arose from the presence of benzoic acid.

I therefore distilled a fresh quantity of cumol with nitric acid, and recollecting the difficulty Mr. Noad experienced in the preparation of toluylic acid, I employed my acid so dilute that even on boiling the mixture no disengagement of red fumes was visible. Having continued the distillation for four or five days the cumol was converted into a crystalline mass, which was strained off from the mother-liquor and recrystallized from water. The properties of this acid distinguished it immediately from nitrobenzoic acid; it was much more soluble in cold and hot water, and might be easily recognised as benzoic acid. Not having sufficient substance for a combustion, I converted the acid into an ammoniacal salt, and precipitated this with nitrate of silver. A white flocculent precipitate was obtained, much more easily soluble in water than nitrobenzoate of silver. On cooling, beautiful crystals separated, having all the properties of benzoate of silver.

The analysis of this salt gave me the following results:—

I. 0·1837 grm. of substance yielded 0·1138 grm. chloride of silver, corresponding to 0·0857 grm. or 46·65 per cent. of silver.

II. 0·1658 grm. yielded 0·0780 grm., or 47·04 per cent. of silver, which numbers correspond with the formula $AgO, C_{14} H_5 O_3$, as may be seen when compared with the theoretical numbers.

| | | Theory. | Found. | |
|---|---|---|---|---|
| | | | I. | II. |
| Benzoic acid . | 113 | 49·35 | | |
| Oxide of silver. | 116 | 50·65 | 50·08 | 50·50 |
| | 229 | | | |

These results were sufficiently near, considering the small amount of substance employed.

From these experiments we see that cumol on being boiled continuously with nitric acid is converted into benzoic and nitrobenzoic acids. The oxidation of cumol is therefore analogous to that of cymol.

$$\underbrace{C_{20}\,H_{14}}_{\text{Cymol.}} + 18O = \underbrace{HO, C_{16}\,H_7\,O_3}_{\text{Toluylic acid.}} + 4CO_2 + 6HO.$$

$$\underbrace{C_{18}\,H_{12}}_{\text{Cumol.}} + 18O = \underbrace{HO, C_{14}\,H_5\,O_3}_{\text{Benzoic acid.}} + 4CO_2 + 6HO.$$

The behaviour of cumol under the influence of the continued action of dilute nitric acid induced me to submit benzol, so nearly related to cumol, to a similar treatment. After having however continued the distillation for about a week I could not obtain an acid from benzol. On employing highly diluted acid, the benzol was gradually converted into nitrobenzol.

Neither benzol nor nitrobenzol is attacked by pure chromic acid, or the oxidizing mixture of bichromate of potash and sulphuric acid. Results quite as unsatisfactory as these were obtained on boiling a solution of hyposulphobenzolic acid with chromic acid or peroxide of manganese.

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CCIV. *On the Preparation of absolute Alcohol, and the Composition of "Proof-Spirit."* *By* Mr. Joseph Drinkwater. (*Communicated by* Professor Graham.)

THE following experiments were undertaken, principally, with a view to determine the relative proportions of anhydrous alcohol and water in revenue proof-spirit, for which purpose it was necessary to procure alcohol in its absolute or pure state.

The processes employed were as follows:—

Carbonate of potash was exposed to a red heat to deprive it of water, and when sufficiently cool was pulverized, and added to ordinary alcohol of specific gravity ·850 at 60° F. till it ceased to dissolve any more; the whole was then allowed to digest twenty-four hours, being frequently agitated, when the alcohol was carefully poured off.

As much fresh-burnt quicklime as was considered sufficient when powdered to absorb the whole of the alcohol, was introduced into a retort, and the alcohol added to it; after digest-

ing forty-eight hours, it was slowly distilled in a water-bath at a temperature of about 180° F.

The alcohol thus obtained was carefully redistilled, and its specific gravity at 60° F. was found in two experiments to be ·7946 and ·7947; agreeing very nearly with the determination of Rudberg, which has been adopted by Gay-Lussac and others, viz. ·7947 at 59° F.

It may be proper to state that the specific gravity was taken with a stoppered bottle, which was always counterpoised by another empty bottle of the same glass and form, placed in the opposite pan of the balance; the capacity of the weighing bottle at 60° F. was exactly 1000·01 grains of distilled water; and it was found on trial that this bottle could be repeatedly filled with the same liquid with no greater variation than one or two hundredths of a grain.

The temperature of the room in which these experiments were made was always brought to 60° F.; and the thermometer used was a standard instrument by Newman, and extremely sensitive (being graduated to one-tenth of a degree); on being plunged into the weighing bottle filled with alcohol it displaced about $4\frac{1}{2}$ grains of that fluid; this portion was replaced from the stock quantity (brought at the time to the proper temperature) by means of a pipette.

With a view however to discover whether it were possible by means of lime to abstract any more water from the alcohol, the retort was again filled with fresh-burned and pulverized quicklime and the same alcohol mixed with it; the mixture was then allowed to digest a whole week at the ordinary temperature of the laboratory, about 60° F. After this time the alcohol was distilled off as before, but was redistilled very slowly, at first at the rate of about one drop in ten seconds (heat of water-bath 165° F.); this was continued till about one-twentieth of the whole had distilled over, the object being to allow any minute quantity of water which the alcohol might still retain to evaporate or diffuse itself into the atmosphere of absolute alcohol above it; the redistillation was then continued rapidly, the heat of the bath being increased to 180° F. till about one-twentieth more had passed over; the receiver was then changed and the remaining part slowly distilled off.

The specific gravity of this alcohol taken twice was ·7944 at 60° F. As a further test of its purity it was divided into two equal parts; one part was again digested on quicklime, and the other on sulphate of copper deprived of water by heat, the method of operation being as follows:—

1st. Some lumps of fresh-burnt quicklime were heated to

a red heat, and in that state quickly pulverized and introduced into the tin boiler of a small still, which was partly immersed in water to prevent the melting of the solder.

This vessel was completely filled with quicklime, and was kept corked till sufficiently cool, when the alcohol was added, but it being comparatively small in quantity the lime appeared perfectly dry; the vessel was then securely corked.

2nd. A quantity of sulphate of copper was exposed to a red heat till completely deprived of water; it was then quickly pulverized and introduced into a small tin boiler, and when cold the alcohol (which was insufficient to cover it) was added, and the vessel closely corked.

These vessels with their contents were kept at the ordinary temperature of the laboratory (about 60° F.) for four days; they were then partly immersed in a water-bath, and kept at a temperature of about 150° F. for forty-eight hours, after which the alcohol was distilled and redistilled with all the precautions before-mentioned; the temperature of the water-bath on the redistillation never exceeded 172° F., and the first tenth part was put aside in each case as possibly impure.

The specific gravities of the alcohol thus obtained were as under:—

| | Alcohol distilled from desiccated sulphate of copper. | Alcohol distilled from quicklime. |
|---|---|---|
| I. . . . | ·79470 | ·79409 |
| II. . . . | ·79472 | ·79412 |

From these experiments it would appear that sulphate of copper, when deprived of water, is not so effective as quicklime in removing the last traces of water from alcohol.

It was observed, however, that in general the specific gravity of the alcohol gradually increased, probably from its hygrometric property, by which it absorbed a minute quantity of moisture from the air on being transferred from one bottle to another; and thinking consequently that a small quantity of moisture might have been abstracted from the atmosphere during the distillation (which was conducted in the usual way), and the specific gravity thus slightly increased, I considered it desirable to make another experiment in which this source of error should be guarded against, by conducting the distillation as much as possible out of contact with the external air, and proceeded as follows.

The different portions of alcohol before obtained were mixed together, when the specific gravity was found to be ·7947; this alcohol was again digested at a temperature of about 150° F. for fourteen days with quicklime, previously

heated to redness, as in the former experiment; it was then slowly distilled out of contact with the external atmosphere by means of a tube which passed from the condenser through a cork into the bottle in which it was to remain (the temperature of the water-bath was 175° F.), and the first tenth part was put aside as possibly containing a minute quantity of water; the remainder was then distilled off at 178° to 180° F.

This alcohol was quickly transferred to a dry retort and redistilled in a similar way (heat of water-bath 172° F.); the first tenth part was put aside, and the remainder kept as being pure anhydrous alcohol, or as free from water as it is possible to obtain it by this process. The specific gravity was taken the next day with all the precautions before mentioned, the alcohol being also kept during the time of transference as much as possible out of contact with humid air, when the results of four trials were as follow:—

Temperature of room 60° F. Barometer 29·810.

| | |
|---|---|
| I. . . . . | ·793836 |
| II. . . . . | ·793806 |
| III. . . . . | ·793798 |
| IV. . . . . | ·793804 |
| Mean . | ·793811 |

A portion of this alcohol was subsequently digested with quicklime for three months, it was then distilled, and its specific gravity was found to be exactly the same as before.

We may therefore conclude with considerable certainty that the number ·79381 expresses the specific gravity of absolute alcohol at 60° F., within a very close degree of approximation.

My attention was next directed to the best method of determining the relative proportions of absolute alcohol and water which exist in legal or revenue proof-spirit.

There is some ambiguity in the wording of the act of parliament 58 Geo. III. c. 28, which defines proof-spirit to be "such as shall at the temperature of fifty-one degrees by Fahrenheit's thermometer weigh exactly twelve-thirteenth parts of an equal measure of distilled water," but the temperature of the water is not stated: there is no doubt however that the temperature of 51° F. was intended to apply to the water as well as to the spirit; therefore taking water at 51° F. as unity, the specific gravity of proof-spirit at that temperature will be ·92308; or raising the temperature of both to 60° F., the specific gravity will be ·91984—the expansions being calculated from Gilpin's Tables *.

* Philosophical Transactions for 1794.

It was found by a few preliminary experiments that the specific gravity ·91984 would lie between a mixture of 49 absolute alcohol + 51 water, and a mixture of $49\frac{1}{2}$ absolute alcohol + $50\frac{1}{2}$ water, all by weight. Mixtures were therefore made in these proportions in an apparatus procured for the purpose, consisting of two light flasks each capable of containing about 2200 grains of water. The alcohol and water were weighed separately in these flasks with the greatest care; after which the flasks were joined without mixing the liquids, the neck of one being ground into the neck of the other for that purpose; the liquids were then thoroughly mixed by transferring them alternately from one flask to the other. The flasks were disconnected when the mixed contents became cool, which were then transferred to a clean and dry well-stoppered bottle, and further secured by tying a piece of caoutchouc over the stopper.

It may also be proper to mention, that when placed in the balance, these flasks were always counterpoised by other empty flasks of the same material, and of very nearly equal size and shape; and to prevent loss from evaporation, a ground glass cap was placed over the mouth of each flask as soon as the exact weight was obtained. The errors of observation could not, I believe, in any case exceed one-hundredth of a grain, as the balance used in these experiments was one of Robinson's best instruments, which was previously adjusted by Newman expressly for the purpose; it was turned with its greatest load by less than one-hundredth of a grain.

The proportions of absolute alcohol and water mixed were as under, all by weight. Temperature of room 60° F. Barometer 29·832.

*First mixture.*—588 grs. alcohol + 612 grs. water, being in the proportion of 49 grs. alcohol + 51 grs. water.

*Second mixture.*—594 grs. alcohol + 606 grs. water, being in the proportion of $49\frac{1}{2}$ grs. alcohol + $50\frac{1}{2}$ grs. water.

After twenty-four hours, the bottles having been frequently shaken, the specific gravities of both mixtures were taken, with all the precautions detailed in the experiments on absolute alcohol: and in order to observe if the full condensation was gradual and required time for its completion, the mixtures were allowed to stand, with occasional agitation, for a further period of twenty-four hours, when the liquids were again weighed. The results were as follows:—

At 24 hours, temperature of room 60° F., barometer 29·630.
At 48 hours, temperature of room 60° F., barometer 29·550.

| *First Mixture.* | | *Second Mixture.* | |
|---|---|---|---|
| I. ·920361 | after standing | I. ·919297 | after standing |
| II. ·920358 | 24 hours. | II. ·919297 | 24 hours. |
| III. ·920361 | after standing 48 hours. | III. ·919307 | after standing 48 hours. |
| Mean ·920360 | | Mean ·919300 | |

It thus appears that both liquids attained a fixed specific gravity within the first twenty-four hours.

If we now express the preceding results by measure, and make the proportion of alcohol a constant quantity in the two mixtures, we have—

| Alcohol and water by weight. Alcohol. | Water. | | Alcohol and water by measure. Alcohol. | Water. | Spec. gravity of the mixtures. |
|---|---|---|---|---|---|
| 49 | + 51 | in the proportion of | 100 | + 82·62105 | ·92036 |
| 49½ | + 50½ | | 100 | + 80·98470 | ·91930 |
| | | Difference . . | | 1·63635 | 106 |

Dividing the difference of the quantities of water by the difference of specific gravity, we get ·015437, the mean quantity of water corresponding to each unit of difference in the specific gravities. But the difference between the specific gravity of proof-spirit and ·91930, one of the observed specific gravities, is 54; therefore we have $54 \times ·015437 = ·8336$, the quantity of water to be added to the spirit of that specific gravity to form proof-spirit, as follows:—

| | Alcohol. | Water. | Specific gravity. |
|---|---|---|---|
| | 100 | + 80·9847 | ·91930 |
| Add water | 100 | ·8336 | 54 |
| Proof-spirit = | 100 | + 81·8183 | ·91984 |

From the foregoing data the following results have been calculated:—

*Composition of Proof-Spirit.*

| Alcohol and water. By weight. | Alcohol and water. By measure. | Specific gravity at 60° F. | Bulk of mixture of 100 measures of alcohol +81·82 water. | Strength per cent. above proof of absolute alcohol. |
|---|---|---|---|---|
| Alcohol. Water. 100 + 103·09 or in 100 49·24 + 50·76 | Alcohol. Water. 100 + 81·82 | ·91984 | 175·25 | 75·25 |

It is remarkable that Dr. A. Steel * arrived at almost the

* Dr. Steel's papers, which contain much valuable information on the specific gravity of spirits, are contained in the 'Records of General Science,' vol. i. pp. 222–255.

same composition for proof-spirit, namely, 49·2 and 50·8, partly by experiment and partly by calculation.

The table of M. Lowitz, showing the quantity of alcohol in spirits of different specific gravities (which is to be found in most chemical works published in this country), also agrees with these experiments at this particular point, although from some experiments which I have had occasion to make, I have found that at other points this table is incorrect; and as it is frequently consulted by chemists, it was considered desirable to make a few mixtures of pure alcohol and water, from which to calculate a more correct table for estimating the quantity of alcohol in mixtures containing not more than 10 per cent. of that liquid.

Eleven mixtures were therefore made, containing exactly $\frac{1}{2}$, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 per cent. by weight of absolute alcohol. These mixtures were made in the same apparatus, and with all the precautions described in the former experiments. They were allowed to stand at least 24 hours with occasional agitation before the specific gravities were taken, and several of them were again taken after a period of 48 and 72 hours, without any sensible variation.

The particulars are set forth in the following table:—

| No. of mixtures. | When the mixtures were made. | | | | | When the specific gravities were taken. | | |
|---|---|---|---|---|---|---|---|---|
| | Alcohol and water mixed. | | Quantity of alcohol per cent. by weight. | Temperature of room. | Height of barometer. | Specific gravity of mixture at 60° F. | Temperature of room. | Height of barometer. |
| | Alcohol. | Water. | | | | | | |
| | grs. | grs. | | | | | | |
| 1. | 5·5 | + 1094·5 | 0·5° F. | 60 | 29·700 | ·99905 | 60° F. | 29·690 |
| 2. | 11·0 | + 1089·0 | 1·0 | 60 | 29·700 | ·99813 | 60 | 29·690 |
| 3. | 22·0 | + 1078·0 | 2·0 | 60 | 29·690 | ·99629 | 60 | 29·500 |
| 4. | 33·0 | + 1067·0 | 3·0 | 60 | 29·718 | ·99454 | 60 | 29·610 |
| 5. | 44·0 | + 1056·0 | 4·0 | 60 | 29·690 | ·99283 | 60 | 29·500 |
| 6. | 55·0 | + 1045·0 | 5·0 | 60 | 29·718 | ·99121 | 60 | 29·610 |
| 7. | 66·0 | + 1034·0 | 6·0 | 60 | 29·742 | ·98963 | 60 | 29·644 |
| 8. | 77·0 | + 1023·0 | 7·0 | 60 | 29·742 | ·98813 | 60 | 29·644 |
| 9. | 88·0 | + 1012·0 | 8·0 | 60 | 29·670 | ·98668 | 60 | 29·800 |
| 10. | 99·0 | + 1001·0 | 9·0 | 60 | 29·670 | ·98527 | 60 | 29·800 |
| 11. | 110·0 | + 990·0 | 10·0 | 60 | 29·800 | ·98389 | 60 | 29·566 |

From the above data the following table has been calculated:—

Table of the quantity of absolute Alcohol by weight contained in mixtures of Alcohol and Water of the following specific gravities:—

| Specific gravity at 60° F. | Alcohol, per cent. by weight. | Specific gravity at 60° F. | Alcohol, per cent. by weight. | Specific gravity at 60° F. | Alcohol, per cent. by weight. | Specific gravity at 60° F. | Alcohol, per cent. by weight. | Specific gravity at 60° F. | Alcohol, per cent. by weight. |
|---|---|---|---|---|---|---|---|---|---|
| 1·0000 | 0·00 | ·9967 | 1·78 | ·9934 | 3·67 | ·9901 | 5·70 | ·9869 | 7·85 |
| ·9999 | 0·05 | ·9966 | 1·83 | ·9933 | 3·73 | ·9900 | 5·77 | ·9868 | 7·92 |
| ·9998 | 0·11 | ·9965 | 1·89 | ·9932 | 3·78 | ·9899 | 5·83 | ·9867 | 7·99 |
| ·9997 | 0·16 | ·9964 | 1·94 | ·9931 | 3·84 | ·9898 | 5·89 | ·9866 | 8·06 |
| ·9996 | 0·21 | ·9963 | 1·99 | ·9930 | 3·90 | ·9897 | 5·96 | ·9865 | 8·13 |
| ·9995 | 0·26 | ·9962 | 2·05 | ·9929 | 3·96 | ·9896 | 6·02 | ·9864 | 8·20 |
| ·9994 | 0·32 | ·9961 | 2·11 | ·9928 | 4·02 | ·9895 | 6·09 | ·9863 | 8·27 |
| ·9993 | 0·37 | ·9960 | 2·17 | ·9927 | 4·08 | ·9894 | 6·15 | ·9862 | 8·34 |
| ·9992 | 0·42 | ·9959 | 2·22 | ·9926 | 4·14 | ·9893 | 6·22 | ·9861 | 8·41 |
| ·9991 | 0·47 | ·9958 | 2·28 | ·9925 | 4·20 | ·9892 | 6·29 | ·9860 | 8·48 |
| ·9990 | 0·53 | ·9957 | 2·34 | ·9924 | 4·27 | ·9891 | 6·35 | ·9859 | 8·55 |
| ·9989 | 0·58 | ·9956 | 2·39 | ·9923 | 4·33 | ·9890 | 6·42 | ·9858 | 8·62 |
| ·9988 | 0·64 | ·9955 | 2·45 | ·9922 | 4·39 | ·9889 | 6·49 | ·9857 | 8·70 |
| ·9987 | 0·69 | ·9954 | 2·51 | ·9921 | 4·45 | ·9888 | 6·55 | ·9856 | 8·77 |
| ·9986 | 0·74 | ·9953 | 2·57 | ·9920 | 4·51 | ·9887 | 6·62 | ·9855 | 8·84 |
| ·9985 | 0·80 | ·9952 | 2·62 | ·9919 | 4·57 | ·9886 | 6·69 | ·9854 | 8·91 |
| ·9984 | 0·85 | ·9951 | 2·68 | ·9918 | 4·64 | ·9885 | 6·75 | ·9853 | 8·98 |
| ·9983 | 0·91 | ·9950 | 2·74 | ·9917 | 4·70 | ·9884 | 6·82 | ·9852 | 9 05 |
| ·9982 | 0·96 | ·9949 | 2·79 | ·9916 | 4·76 | ·9883 | 6·89 | ·9851 | 9·12 |
| ·9981 | 1·02 | ·9948 | 2·85 | ·9915 | 4·82 | ·9882 | 6·95 | ·9850 | 9·20 |
| ·9980 | 1·07 | ·9947 | 2·91 | ·9914 | 4·88 | ·9881 | 7·02 | ·9849 | 9·27 |
| ·9979 | 1·12 | ·9946 | 2·97 | ·9913 | 4·94 | ·9880 | 7·09 | ·9848 | 9·34 |
| ·9978 | 1·18 | ·9945 | 3·02 | ·9912 | 5·01 | ·9879 | 7·16 | ·9847 | 9·41 |
| ·9977 | 1·23 | ·9944 | 3·08 | ·9911 | 5·07 | ·9878 | 7·23 | ·9846 | 9·49 |
| ·9976 | 1·29 | ·9943 | 3·14 | ·9910 | 5·13 | ·9877 | 7·30 | ·9845 | 9·56 |
| ·9975 | 1·34 | ·9942 | 3·20 | ·9909 | 5·20 | ·9876 | 7·37 | ·9844 | 9·63 |
| ·9974 | 1·40 | ·9941 | 3·26 | ·9908 | 5·26 | ·9875 | 7·43 | ·9843 | 9·70 |
| ·9973 | 1·45 | ·9940 | 3·32 | ·9907 | 5·32 | ·9874 | 7·50 | ·9842 | 9·78 |
| ·9972 | 1·51 | ·9939 | 3·37 | ·9906 | 5·39 | ·9873 | 7·57 | ·9841 | 9·85 |
| ·9971 | 1·56 | ·9938 | 3·43 | ·9905 | 5·45 | ·9872 | 7·64 | ·9840 | 9·92 |
| ·9970 | 1·61 | ·9937 | 3·49 | ·9904 | 5·51 | ·9871 | 7·71 | ·9839 | 9·99 |
| ·9969 | 1·67 | ·9936 | 3·55 | ·9903 | 5·58 | ·9870 | 7·78 | ·9838 | 10·07 |
| ·9968 | 1·73 | ·9935 | 3·61 | ·9902 | 5·64 | | | | |

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## CCV. *On Cochineal* (Coccus Cacti). *First Memoir.* *By* Warren De la Rue, *Esq.*

THE beautiful theoretical results which have been lately obtained by a closer examination of indigo blue and its products of decomposition, made it desirable to undertake similar investigations with other colouring matters. I made choice of the colouring principle of cochineal (*Coccus Cacti*), hoping that a detailed research might not only prove of interest in a scientific point of view, but also throw some light on its practical applications, and the more so, as the recent investigations of Preisser had seemed to point out a very close

analogy in the chemical properties of a variety of colouring matters with indigo blue.

Before entering into the detail of my experiments, I think it desirable to give a brief outline of the results obtained by the chemists who have hitherto worked on this subject.

Dr. Jean Frédéric John, in a quarto volume translated from the German and entitled *Tableaux Chimiques du Règne Animal*, appears to have published the first analysis of cochineal: he does not describe his method, but merely states that it contains the following per-centage:—

| | |
|---|---|
| Colouring principle (semi-solid, soluble in water and alcohol) . . . . . | 50·00 |
| Gelatine . . . . . | 10·50 |
| Waxy fat . . . . . | 10·00 |
| Modified mucus . . . . . | 14·00 |
| Membrane . . . . . | 14·00 |
| Alkaline phosphates and chlorides, phosphate of lime, phosphate of iron, and phosphate of ammonia . . . . . | 1·50 |
| | 100·00 |

Pelletier* and Caventou, in a very long memoir read before the Institut de France in 1818, have gone very elaborately into the examination of cochineal and obtained many interesting results. In analysing this substance they employed the following process:—They removed the fatty bodies by boiling æther, in which they found the colouring matter but slightly soluble; these fatty substances, recovered by distilling off the æther, were considered to consist of stearine, oleine, and an aromatic acid, from which latter substance it was difficult to remove the adhering colouring matter.

The cochineal, exhausted with æther, was treated with alcohol of 40° Beaumé, which dissolved the colouring matter, together with a small quantity of fatty and nitrogenous substances.

On cooling, and by spontaneous evaporation, they obtained a granular red residue of a semi-crystalline appearance, and which they considered to be the colouring matter contaminated still with nitrogenous matter (*matière animalisée*) and some fatty bodies, the greater part of which remained undissolved in strong cold alcohol; by repeating the operation once or twice they considered that the substance was obtained almost in a state of purity. To remove the last traces of foreign matter it was dissolved in strong alcohol, and

* *Annales de Chimie et de Physique*, sér. 2, tome viii. p. 250. *Journal de Pharmacie*, sér. 2, tome iv. p. 193.

an equal volume of æther added, which precipitated the colouring matter and retained the fat, which was still adhering to it. The colouring matter thus purified they named carmine (*carminium*), and described as being very soluble in water, from which it did not crystallize, more or less soluble in alcohol, according to its strength, and quite insoluble in æther and the fixed and volatile oils. Acids did not precipitate it from its aqueous solution if free from animal matter. They found hydrochloric and sulphuric acid to decompose it; the latter with elimination of carbon. By the action of nitric acid they obtained an acid in prismatic crystals resembling oxalic acid, but differing in some of its properties.

On heating the "carmine" it intumesced and gave off carburetted hydrogen, a considerable quantity of oily substances, a little acid water, but no trace of ammonia. Chlorine and iodine decomposed it; the alkalies in the commencement produced merely a change in colour, turning it violet, but by the assistance of time or heat they effected a complete alteration. They found an aqueous solution of "carmine" to exhibit the following comportment with reagents.

Of the alkaline earths, lime only produced a precipitate; hydrate of alumina showed a marked affinity, absorbing the whole of the colouring matter from an aqueous as well as an alcoholic solution; the presence of alum prevented this reaction: iron, copper, and silver salts were without reactions; terchloride of gold destroyed the colour; neutral salts of lead merely changed it to violet, except the neutral acetate, which precipitated it, the free acetic acid retaining a little of the compound in solution; the colouring matter could be recovered by decomposing the lead compound with hydrosulphuric acid. The nitrate of mercury gave a purple, and the pernitrate a scarlet-red precipitate; the bichloride no precipitate; chloride of tin gave a violet precipitate; the bichloride changed the colour to scarlet without causing a precipitate. Albumen and gelatine had no marked action, but if precipitated by reagents the colouring matter was carried down.

In a later communication (1832), Pelletier* gave the composition of the colouring matter as prepared by himself and Caventou. In a previous qualitative examination they had failed to exhibit the presence of nitrogen which M. Pelletier now detected. The substance was dried *in vacuo* at a gentle heat to remove every trace of alcohol and æther, and burnt with oxide of copper it yielded—

* *Annales de Chimie et de Physique*, sér. 2, tome li. p. 194.

| | |
|---|---|
| Carbon . . . . . | 49·33 |
| Hydrogen . . . . . | 6·66 |
| Nitrogen . . . . . | 3·56 |
| Oxygen . . . . . | 40·45 |
| | 100·00 |

M. Pelletier stated, however, that he did not greatly rely on the correctness of this analysis.

After alcohol had dissolved out all the colouring matter removable by it, they extracted the last traces, by repeatedly washing the residue with boiling water, and along with it a little fatty and some nitrogenous matter; the residue was a brownish transparent mass. The later decoctions, containing no red colouring matter, left likewise on evaporation a brownish transparent mass, which they considered identical with the organic residue of the insect. This animal matter had, according to them, some analogy with gelatine, but differed in many of its properties, as it did also from albumen and fibrine, they therefore considered it as peculiar to the cochineal insect; the alkalies and ammonia dissolved it readily; chlorine precipitated it; all acids and acid salts precipitated it, as also acetate of lead, salts of tin and copper, and nitrate of silver; and they considered the latter reagent as a good test of the purity of the colouring matter, as it did not precipitate the latter if free from nitrogenous substances. If the colouring matter were contaminated with nitrogenous substances, all the salts which precipitated the latter carried down likewise some of the colouring matter.

An examination of the ashes showed the presence of phosphate of lime, carbonate of lime, chloride of potassium, and phosphate of potash, to the extent of 0·7 per cent.

In the second part of the memoir they went into the theory of the technical applications of the colouring matter: this having no reference to the present subject, I do not think it necessary to reproduce it here.

M. Lassaigne, in 1819*, examined Kermes (*Coccus ilicis*), an insect common in the South of Europe, and employed as a red dye before the discovery of America, and obtained by following the methods of Pelletier and Caventou, substances agreeing in their properties with the analogous ones found in cochineal.

M. F. Preisser†, in an elaborate paper on the origin and nature of colouring matters, has again drawn the attention of chemists to the subject. This gentleman, from a study of a variety of colouring substances, comes to the conclusion that all resemble indigo in its behaviour with reducing agents.

* *Journal de Pharmacie*, sér. 2, tome v. p. 435. † *Ibid.* p. 191.

He affirms that he obtained by the action of hydrosulphuric acid on the lead compounds of a great number of organic colouring matters, substances bearing the same relation to the original colouring matters as white indigo does to blue indigo. In order to obtain the colourless modification of the colouring matter of cochineal, he adds what he terms "hydrate of oxide of lead" to an aqueous decoction of cochineal, the fats being previously removed by æther. The colouring matter is entirely removed by the so-called oxide of lead, which is nothing but a basic nitrate of lead, $2(3PbO, NO_5)+3HO$. The lead compound suspended in water (hot?) was decomposed by a stream of hydrosulphuric acid; the nearly colourless filtrate deposited on cooling needles of a pale yellow colour, which became perfectly white by washing with æther and pressing between bibulous paper; these crystals, which, according to his statement, are soluble in water and alcohol, but less so in æther, assume in contact with the atmosphere the purple-red of the colouring matter of cochineal. He moreover asserts that his colourless modification gives a white lead salt on adding acetate of lead to its aqueous solution, and that this assumes a purple colour in contact with the air.

He proposes to give the name carmine, hitherto applied to the red colouring matter, to the white crystals, and to designate the red substance by the name "Carméine."

The statements of Preisser, generalizing most beautifully under one head the chemical character of all colouring matters, making indigo as it were the prototype of them all, could but induce other chemists to work out more in detail the relations cursorily pointed out in the memoir of this chemist. Unfortunately a careful repetition of these experiments has not confirmed the basis on which his theory reposes.

M. A. E. Arppe repeated Preisser's experiments on the colouring matter of cochineal*. He found that by proceeding in the manner described by Preisser that he could only obtain a red solution, which on evaporation was converted into white crystals of oxalic acid by the nitric acid derived from the basic lead salt.

Arppe now prepared a pure oxide of lead by precipitating acetate of lead with potash. He found that this would not take down the colouring matter in the cold, but by boiling it is carried down as a blue lake, which he decomposed by hydrosulphuric acid; the supernatant liquor was nearly colourless, the colouring matter he found adhered with great obstinacy to the sulphide of lead, from which water, alcohol and ammonia failed to separate it; but sulphide of ammo-

* Liebig's *Annalen*, vol. lv. p. 101.

nium and acids rendered it perceptible. He likewise tried to obtain the colouring matter in a state of purity by precipitating with hydrated oxide of lead an aqueous decoction of cochineal (previously purified from nitrogenous substances by nitrate of silver). On treating the precipitate by hydrosulphuric acid, he obtained a red liquor of *strongly acid reaction*, the acid of which was not derived from the lead salt: on evaporation it left a dark red mass, emitting the smell of burnt sugar. Wishing to separate the acid, which he thought contaminated the colouring matter, he prepared a strong aqueous decoction of cochineal, and after separating the nitrogenous matter by means of nitrate of silver, filtering, and then saturating by ammonia, and afterwards adding the hydrated oxide of lead, he found that the supernatant ammoniacal liquor, which was nearly colourless, yielded by evaporation an acid liquid; and on decomposing the lead lake with hydrosulphuric acid, he obtained a liquid slightly coloured (the colouring matter adhering to the sulphide of lead), which was likewise acid. From this he concluded that the colouring matter had not up to that period been obtained in a state of purity.

*Microscopic Examination of Living Cochineal.*

By the kindness of Sir James Clark, who furnished me with specimens of the living insect, I have been enabled to examine the physical characters of the colouring matter as it exists in the organism of this little insect before it is subjected to the process of drying for commerce. On examination by the microscope, the white dust which covers the insect and the adjacent parts of the cactus leaves, on which it feeds, has all the characters of an excrement; it has a curled cylindrical form, is of very uniform diameter and of a white colour. On removing the powder with a little æther and piercing the side of the little creature, a quantity of a purplish red fluid exudes, which contains the colouring matter in minute granules assembled round a colourless and larger nucleus, and these groups float in a colourless fluid. It is evident from this, that, whatever may be the function of the colouring matter, it has a distinct and marked form, and does not pervade as a mere tint the fluid portion of the insect.

*Separation of the Colouring Matter.*

It became evident from a few preliminary experiments that the investigation would be greatly facilitated by the employment of a large quantity of material; and as in the course of the inquiry different methods were adopted for the prepara-

tion of the colouring matter, capital letters will be used to designate the various preparations.

A. About 3 lbs. of ground cochineal (technically known as shelly black) was introduced into 15 gallons of boiling distilled water, and the mixture maintained at that temperature for twenty minutes; the decoction, strained through a sieve, was allowed to subside for a quarter of an hour and then decanted off; whilst still hot the transparent liquid was mixed with basic nitrate of lead, added with caution to avoid excess; a fine purple lake was thus obtained, the supernatant liquor retaining only a pale buff tinge. After decantation of the supernatant liquor, the lake was thrown on a cloth filter and washed with distilled water until the filtrate gave but a slight opalescence with chloride of mercury, which was found to be a test for the presence of nitrogenous matter. The lead lake was then suspended in distilled water and treated with a copious stream of hydrosulphuric acid, when a precipitate of sulphide of lead and a deep red supernatant liquid was obtained; on stirring the liquid this colour almost disappeared, the colouring matter being evidently absorbed by the sulphide, agreeing perfectly with Arppe's observation. A fresh stream of gas reproduced the colour, which was again absorbed on stirring; after continuous treatment with hydrosulphuric acid, the lead lake being completely decomposed, the filtered liquid was evaporated in a water-bath to a syrupy consistence, and the evaporation finished as far as possible at a temperature of 38° C. The semi-solid substance thus obtained was of a deep purple colour, had a strongly acid reaction, and evolved the smell of burnt sugar, as noticed by Arppe. The weight of this substance, which I call crude carminic acid, was $3\frac{1}{2}$ ozs., and 1 oz. more was obtained from the residue by similar treatment.

B. On repeating the same process the whole product was lost. An excess of the basic nitrate having been employed, the nitric acid set free by the hydrosulphuric acid caused a violent decomposition, with evolution of nitrous fumes, as soon as the carminic acid arrived at a pasty consistence; this agrees also with Arppe's experience.

C. In this operation a decoction of cochineal, made in the described manner, was precipitated with a solution of acetate of lead acidulated with acetic acid (six parts by weight of crystallized acetate, and one part of strong acetic acid). The resulting lead lake, being very bulky, was washed by decantation with boiling distilled water, collected on a filter, dried in a current of warm air, and finely powdered; 17 ozs. of *crude carminate of lead* were thus obtained.

D. Half a pound of cochineal was boiled with five pints of alcohol, spec. grav. ·830. The filtered tincture deposited on cooling a granular precipitate, consisting chiefly of fatty matter retaining a portion of colouring matter; on concentrating the tincture by distillation a further quantity was deposited, which was filtered off; the filtrate was evaporated to dryness *in vacuo*, when after eight weeks a gummy residue was obtained. This mass dissolved with great difficulty in a large quantity of absolute alcohol, a red flocculent substance consisting chiefly of nitrogenous matter remaining undissolved. The alcoholic solution filtered off from this deposit, concentrated by distillation and finally evaporated *in vacuo* over sulphuric acid, dried to a tenacious semi-solid mass, covered with a colourless oily fluid, and containing crystalline particles of a solid fat. After removal of the fats by means of æther, this mass was digested in water at 38° C., which partly dissolved it with a fine red colour, leaving a brown mass of resinous aspect behind, more of which deposited on the cooling of the coloured liquid; the decoction was now evaporated to the consistence of a syrup, and finally dried *in vacuo* over sulphuric acid.

These are all the processes employed to *extract* the colouring matter from the cochineal; I may here remark, before entering on the details of its further purification, that I obtained other substances on evaporating the mother-liquors from which the colouring matter had been separated by lead salts, which will be hereafter described.

*Purification of the Carminic Acid.*—In my first attempts to purify the colouring matter I proceeded in the following way:—An aqueous solution of the crude carminic acid (A) was precipitated with acetate of lead, the precipitate of carminate of lead well-washed and decomposed by hydrosulphuric acid; the red supernatant liquid was first concentrated on the water-bath and finally dried *in vacuo*; a highly hygroscopic purple residue was thus obtained.

I could not, by whatever means I adopted, effect the decolorization of the colouring principle. In several attempts I heated the solution for some hours to 100° C., keeping up a continuous current of hydrosulphuric acid, and in other experiments a stream was made to pass for several days through the disengaged colouring matter, but without the slightest change in its aspect. From these experiments, made with the greatest care and at several periods, I am led to the same conclusion as Arppe, that Preisser must have been mistaken in his results, and I regret that I cannot throw any light on the probable cause of his error.

Several combustions of the carminic acid thus purified were made, the resulting numbers however became useless by the subsequent observation that this acid was by no means pure. A sufficient quantity being incinerated left a residue of acid reaction, which was suspected to contain phosphoric acid. Carminic acid burning only with great difficulty, it was reconverted into carminate of lead, the oxide of lead dissolved out of the residue obtained after fuming by acetic acid, which left a white residue of metaphosphate of lead, together with a little lead. The white residue was soluble in dilute nitric acid, and exhibited, when treated before the blowpipe, the characters of metaphosphate of lead; other tests likewise confirmed the presence of phosphoric acid. It will hereafter be seen that the process of extracting the colouring matter by alcohol (D) does not exclude the phosphoric acid, which in all probability existed in the colouring matter analysed by Pelletier. It is further evident that the presence of phosphoric acid explains most satisfactorily the facts observed by Arppe.

*a.* In order to separate the phosphoric acid, another portion of crude carminic acid (A) was precipitated with acetate of lead. Three-fourths of the carminate of lead produced were decomposed by hydrosulphuric acid and evaporated to dryness in the way already mentioned. The dry mass being dissolved in cold absolute alcohol, and filtered from a slight flocculent brownish residue, was heated to ebullition in a water-bath and mixed with the remaining fourth of the carminate of lead, which had been previously reduced to a fine powder; the ebullition was continued for a few hours. In this method the free phosphoric acid combined with the lead, liberating an equivalent proportion of carminic acid, which was taken up by the alcohol. The alcoholic solution was filtered whilst hot, concentrated by distillation, and then evaporated *in vacuo* in the presence of sulphuric acid; it dried into a granular mass of a deep purple-brown colour, detaching itself spontaneously from the sides of the vessel, and on examination by the microscope was found to be a beautiful transparent crimson substance, exhibiting only slight, if any, signs of crystalline structure; by pulverization it became of a fine scarlet colour; it left a mere trace of ash, and was found to be perfectly free from phosphoric acid. It was highly hygrometric*.

* In consequence of this it was found convenient to dry the carminic acid intended for analysis in little stoppered tubes in the air-pump, as the stopper could be rapidly inserted after desiccation, and access of air effectually prevented.

Burnt with chromate of lead,—

I. ·4647 grm. gave ·9096 grm. carbonic acid and ·2175 grm. water.

II. ·4630 grm. gave ·9105 grm. carbonic acid and ·2140 grm. water.

For the latter analysis I am indebted to my friend Mr. Nicholson.

*b.* A second preparation of carminic acid was made by operating on the crude carminate of lead (C) and treating the resulting crude carminic acid in the manner just described for the preparation *a*. It left on incineration 0·2 per cent. of ash (·1609 grm. giving ·0003 grm. ash), which was neglected in the following analyses:—

III. ·3710 grm. gave ·7316 grm. carbonic acid and ·1710 grm. water.

IV. ·3685 grm. gave ·7235 grm. carbonic acid and ·1722 grm. water.

*c.* To effect the purification of the carminic acid (D) obtained by digesting cochineal in alcohol, it was dissolved in water and precipitated by acetate of lead; the filtrate was found to contain nitrogenous matter, and the carminate of lead to be contaminated with phosphate of lead; it was therefore treated in the manner already detailed.

V. ·3925 grm. of this substance gave ·7658 grm. carbonic acid and ·1780 grm. water.

*d.* A fourth preparation of carminic acid was obtained by substituting phosphoric acid for hydrosulphuric in the decomposition of the crude carminate of lead (C), and evaporating the carminic acid to dryness in contact with a fresh portion of carminate of lead; this did not however separate entirely the phosphoric acid, it was therefore redissolved in boiling absolute alcohol, and maintained some time at that temperature with more carminate of lead. On analysis—

VI. ·3805 grm. gave ·7530 grm. carbonic acid and ·1848 grm. water.

Pelletier having obtained in his analysis of "carmine" (carminic acid) as much as 3·56 per cent. of nitrogen, all the before-cited preparations of carminic acid were carefully examined qualitatively for nitrogen by heating with soda-lime, and without exception gave indications of its presence; in most cases but a mere trace was found, but I thought it necessary notwithstanding to make a few quantitative determinations, especially as M. Berzelius* had pointed out the improbability of it being an essential constituent.

* *Traité de Chim.* t. iii. p. 808. Brussels, edit. 1839.

The last preparation (*d*) appearing to contain more than any of the others, it was chosen and burnt with soda-lime.

It was indispensable in experiments of this nature to test the purity of the soda-lime as regarded the absence of ammonia. A tube having 9 inches of its length filled with soda-lime was heated to redness, just as in a nitrogen determination; the hydrochloric acid, being treated with bichloride of platinum in the usual manner, gave 7·5 milligrammes of ammonio-chloride of platinum; and a repetition of the experiment gave a similar result. This allowance has been made on all the nitrogen determinations by soda-lime.

·5938 grm. carminic acid (*d*) gave ·0717 grm. ammonio-chloride of platinum = 0·76 per cent. of nitrogen.

This quantity of nitrogen could not be supposed to belong to the composition of the colouring matter, but was evidently due to some foreign substance, and not improbably to ammonia. In order to purify the carminic acid still more, the same specimen (*d*) was dissolved in a small quantity of boiling absolute alcohol and the filtered solution mixed with three times its bulk of anhydrous æther; a splendid scarlet precipitate was immediately produced, which absorbed water rapidly from the atmosphere, and agglutinated into a dark purple mass; when dried it weighed 0·3 grm. (*e*). The filtrate, which was of a pale orange-red colour, left on evaporation 0·5 grm of carminic acid (*f*).

·2635 grm. (*e*) burnt with soda-lime gave ·0637 grm. ammonio-chloride of platinum = 1·52 per cent of nitrogen.

·4732 grm. (*f*) gave ·0150 grm. ammonio-chloride of platinum = 0·2 per cent. of nitrogen.

We have therefore (*e*) 0·3 grm. found to contain by analysis 1·5 per cent. nitrogen, and (*f*) 0·5 grm. 0·2 per cent., $\frac{(3 \times 1{\cdot}5) + (5 \times 0{\cdot}2)}{8} = {\cdot}69$ average per cent., which agrees closely with ·76, found previous to treatment with æther.

*g.* Another preparation of carminic acid was obtained by precipitating crude carminic acid with acidulated acetate of copper, which salt was found to carry down the carminic acid, and to leave in solution by far the greater portion of the phosphoric acid. The carminate of copper, which occupied a long time in washing, was collected and decomposed by hydrosulphuric acid. The filtrate was evaporated to dryness, dissolved in boiling absolute alcohol, filtered, concentrated by distillation, and again evaporated to dryness *in vacuo*. It still contained a trace of phosphoric acid. On evaporating the mother-liquor and filtering, from an impure carminate of copper which deposited as the acetic acid was driven off, and

again concentrating to dryness, a brown mass was obtained, which on incineration left a greenish-white very hygrometric ash, in which phosphoric acid, soda and copper were found. Burnt with chromate of lead—

VII. ·4020 grm. carminic acid (*g*) gave ·7842 grm. carbonic acid and ·1662 grm. water.

This acid however still retained some impurities: on incineration it left 0·4 per cent. of ash (·5489 grm. giving ·0022 grm. ash), and examined for nitrogen it gave the following numbers:—

·4731 grm. burnt with soda-lime gave ·0150 grm. ammonio-chloride of platinum = 0·2 per cent. of nitrogen.

*h.* In order to separate these impurities the greater portion was dissolved in boiling absolute alcohol, and filtered from a slight residue; the remainder, about an eighth, was converted into carminate of lead and digested with the boiling alcoholic solution for some hours; the alcoholic tincture filtered off whilst hot and mixed with about six times its volume of anhydrous æther; this threw down a bulky precipitate of a fine red colour, which was separated by filtration and the filtrate concentrated in a retort, and finally evaporated to dryness *in vacuo* (*h*).

*i.* The precipitate retained on the filter was dried *in vacuo*, then dissolved in as small a quantity of alcohol as possible, and again mixed with a large quantity of æther; this determined a precipitate which was no longer of a fine red but of a brown colour, and on re-solution and similar treatment it diminished in quantity and became darker in colour, leaving the colouring matter in solution. From the filtrates a quantity of carminic acid (*i*) was obtained on evaporating to dryness *in vacuo*. It therefore appears that the æther precipitates a nitrogenous body which carries down with it variable quantities of carminic acid, according as a larger or smaller relative proportion is present. The carminic acid (*h*) was found to be free from phosphoric acid as well as nitrogen.

·3003 grm. burnt with soda-lime gave ·0015 grm. ammonio-chloride of platinum = 0·03 per cent. of nitrogen.

From this analysis I venture to assert that the colouring principle of cochineal contains no nitrogen, thus fully confirming the anticipation of Berzelius. We can now understand from the preparation of the specimen of carminic acid (*e*), that the method employed by Pelletier for the preparation of the substance he analysed was calculated to accumulate all the nitrogenous matter contained originally in his alcoholic decoction; a fact which fully explains the large amount of nitrogen he obtained in his analysis.

An analysis of the carminic (*h*) acid by chromate of lead gave from—

VIII. ·3167 grm. ·6203 grm. carbonic acid and ·1402 water.

The following table exhibits the per-centage results deduced from the foregoing analyses: the specimens were all dried over sulphuric acid *in vacuo*, with the exception of analysis VII., in which the carminic acid was dried at 100° C.

| | I. | II. | III. | IV. | V. | VI. | VII. | VIII. | Mean. |
|---|---|---|---|---|---|---|---|---|---|
| Carbon ... | 53·38 | 53·63 | 53·78 | 53·55 | 53·21 | 53·97 | 53·20 | 53·42 | 53·51 |
| Hydrogen | 5·20 | 5·14 | 5·12 | 5·19 | 5·04 | 5·39 | 4·59 | 4·92 | 5·07 |

By the analysis of a copper salt of carminic acid hereafter to be mentioned, it became probable that carminic acid might still retain, when only dried *in vacuo*, a portion of the solvents employed; a presumption which was supported by the analysis VII., in which the substance analysed had been dried at 100° C., and which gave a smaller per-centage of hydrogen. A portion of carminic acid (*i*), being first dried *in vacuo*, and then heated to a temperature of 121° C., was found to yield a small quantity of acetic acid, and was not altered in its properties, which were not in fact changed even at a temperature of 136° C.

In the following analyses the carminic acid, previously dried *in vacuo* * and then at a temperature of 120° C., gave, on burning with chromate of lead, the following results:—

IX. ·3347 grm. (*h*) gave ·6648 grm. carbonic acid and ·1381 grm. water.

X. ·3583 grm. (*i*) gave ·7108 grm. carbonic acid and ·1504 grm. water.

These analyses give the following per-centage quantities:—

| | IX. | X. |
|---|---|---|
| Carbon . . . | 54·17 | 54·10 |
| Hydrogen . . | 4·58 | 4·66 |

The analysis IX. being of the same preparation as had served for analysis VIII., it is fair to presume that all the other specimens of carminic acid would have given the same per-centage quantities as the specimen (*h*) if dried at 120° C., as this particular specimen, dried *in vacuo*, yielded numbers in close accordance with the mean of the other analyses.

These numbers converted into the most simple expression lead to the following formula, $C_{14}\,H_7\,O_8$; but an analysis of a copper salt renders it probable that this formula has to be

* The carminic acid fuses if exposed to a temperature of 120° C. without having been previously dried.

doubled, and that the composition of carminic acid is expressed by the formula,

$$C_{28}\ H_{14}\ O_{16},$$

as may be seen from the following table containing the comparison of the theoretical per-centages with the mean of analyses IX. and X.

| | | Theory. | Experiment. |
|---|---|---|---|
| $C_{28}$ . | 168 | 54·19 | 54·13 |
| $H_{14}$ . | 14 | 4·52 | 4·62 |
| $O_{16}$ . | 128 | 41·29 | 41·25 |
| | 310 | 100·00 | 100·00 |

From the foregoing experiments, it seems that the best method of obtaining pure carminic acid is to precipitate the aqueous decoction by acetate of lead; to decompose the washed carminate of lead by hydrosulphuric acid, and to throw down the carminic acid once more by acetate of lead, previously mixed with acetic acid; to decompose the carminate of lead by hydrosulphuric acid; to evaporate to dryness and redissolve the carminic acid in absolute alcohol; then to digest the alcoholic tincture with carminate of lead; and lastly, to precipitate the trace of nitrogenous matter by æther, the pure carminic acid is obtained from the filtrate.

As thus prepared, carminic acid has the following properties. It is a purple brown friable mass, transparent when viewed by the microscope, and pulverizing to a fine red powder; soluble in water and alcohol in all proportions, very slightly soluble in æther, which does not however precipitate it from its alcoholic solution if free from nitrogenous matter. It is soluble without decomposition in concentrated hydrochloric and sulphuric acids. It is decomposed by chlorine, iodine and bromine, which change its colour to yellow, and the latter on warming or by standing gives a yellow precipitate soluble in alcohol. Nitric acid decomposes it even if highly diluted: I shall have occasion to refer to this decomposition presently. It bears a temperature of 136° C. without decomposition; on gradually increasing the temperature a quantity of an acid liquor is produced, and at a red heat it intumesces and gives off a small quantity of red fumes, which condense: it gives no trace of oily matter.

The aqueous solution has a feeble acid reaction; it does not absorb oxygen. A volume of this gas contained in a tube with carminic acid over mercury did not change by absorption after exposure for several months. The fixed alkalies and ammonia give no precipitate in the aqueous solution, merely changing its colour to purple; in the alcoholic tincture they

produce purple precipitates; all the alkaline earths produce purple precipitates; sulphate of alumina gives no precipitate, but on addition of a drop of ammonia the carminic acid is immediately taken down as a beautiful crimson lake; acetates of lead, copper, zinc and silver give purple precipitates; the latter is immediately decomposed, and silver deposited; the nitrates of lead, mercury and silver reddish precipitates; protochloride and bichloride of tin no precipitates, but change the colour to a deep crimson.

The acid character of carminic acid being so very little pronounced, I met with considerable difficulties in determining its atomic weight; it is only with great reserve that I bring forward the formula before cited. Several attempts were made to produce soda, baryta, lead and copper compounds, but it was only with the copper salt that I obtained results agreeing in different preparations.

It seems that carminic acid attaches itself to salts, for it was found that the precipitants could be removed from the precipitates only with the greatest difficulty. I omit several soda, baryta and lead determinations which have not led to any satisfactory result, and confine myself to the statement of the result of the analysis of the copper compound. It was obtained by acidulating an aqueous solution of pure carminic acid with acetic acid, and then precipitating by the cautious addition of acetate of copper, so as to leave an excess of carminic acid in the liquid. The precipitate was well-washed by decantation (by which a great loss was sustained) and dried. It formed into masses of a bronze colour, very hard and difficult to powder. Two specimens were prepared at different times (*a* and *b*).

I. ·2800 grm. (*a*) dried at 100° C. left, after ignition and treatment with nitric acid and re-ignition, ·0330 grm. oxide of copper.

II. ·3782 grm. (*b*) dried at 100° C. gave ·0426 grm. oxide of copper.

III. ·4702 grm. (*b*) dried at 100° C. gave on burning with chromate of lead ·8210 grm. carbonic acid and ·1743 grm. water.

These numbers lead to the following per-centage results:—

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . . | ... | ... | 47·62 |
| Hydrogen . . | ... | ... | 4·12 |
| Oxide of copper | 11·78 | 11·27 | |

agreeing closely with the formula, $C_{28}H_{14}O_{16}$, CuO, as will be seen from a comparison of the theoretical and experimental numbers.

| | | | Calculated. | Found. |
|---|---|---|---|---|
| Carbon . . . | 28 | 168 | 48·05 | 47·62 |
| Hydrogen . . | 14 | 14 | 4·01 | 4·12 |
| Oxygen . . . | 16 | 128 | 36·61 | 36·74 |
| Oxide of copper | 1 | 39·6 | 11·33 | 11·52 |
| | | 349·6 | 100·00 | 100·00 |

*Action of Nitric Acid on Carminic Acid.*

*Nitrococcusic Acid.*—When acting with nitric acid on "carmine" (carminic acid), MM. Pelletier and Caventou obtained white acid crystals resembling oxalic acid, but differing from this acid in several of its properties. M. Arppe found that the acid produced was oxalic acid. In my experiments I obtained the following results:—One pound and a half of crude carminic acid was gradually introduced into ten pounds of nitric acid, spec. grav. 1·4, and digested at a moderate heat; a violent evolution of nitrous fumes succeeded each addition of the carminic acid; after the whole quantity had been introduced and the action had somewhat subsided, the mixture was transferred into a smaller vessel and the action continued at the boiling-point for about two hours; by this time the greater part of the nitric acid had evaporated, and on withdrawing the vessel from the fire and allowing the mixture to cool, a crystalline cake was obtained, which on examination was found to consist partly of a new acid and partly of oxalic acid. To separate the oxalic acid, it was dissolved in a large quantity of boiling water and treated with nitrate of lead as long as any precipitate formed; this was collected and decomposed by boiling with dilute sulphuric acid; the filtrate from the sulphate of lead yielded a large quantity of prismatic crystals of oxalic acid, which were obtained perfectly white and pure after two or three crystallizations with the aid of a little animal charcoal.

The yellow liquid filtered from the oxalate of lead was concentrated and separated from a fresh portion of oxalate which deposited on concentration, the evaporation was then continued until a large quantity of crystals formed; the solution on cooling deposited a very bulky mass of yellow rhombic prisms, which were drained and dried, and re-dissolved in a sufficient quantity of boiling water, which on cooling deposited the acid (for which I propose the name of nitrococcusic acid) in beautiful crystals free from any lead salt; it was recrystallized twice more, by which means it was obtained perfectly pure.

Several preparations were made, sometimes using pure car-

minic acid, at other times carminate of lead, with similar results.

The analyses of four different preparations dried at 100° C. gave, on burning with chromate of lead (unless otherwise stated), the following numbers:—

I. ·3152 grm. (*a*) gave ·3892 grm. carbonic acid and ·0561 grm. water.

II. ·2500 grm. (*a*) gave ·3080 grm. carbonic acid and ·0445 grm. water.

(For this analysis I am indebted to Mr. Nicholson.)

III. ·3068 grm. (*a*) gave ·3820 grm. carbonic acid and ·0502 grm. water.

IV. ·4498 grm. (*b*) gave ·5626 grm. carbonic acid and ·0757 grm. water.

V. ·4461 grm. (*c*) gave ·5515 grm. carbonic acid and ·0777 grm. water.

VI. ·4503 grm. (*d*) gave, on being burnt with oxide of copper, ·5585 grm. carbonic acid and ·0757 grm. water.

VII. ·4796 grm. (*c*) gave, on being burnt with oxide of copper, and a layer of copper twelve inches long used so as to completely decompose the binoxide of nitrogen, ·5882 grm. carbonic acid and ·0815 grm. water.

The foregoing analyses lead to the following per-centage quantities:—

| | I. | II. | III. | IV. | V. | VI. | VII. |
|---|---|---|---|---|---|---|---|
| Carbon . | 33·67 | 33·60 | 33·95 | 34·11 | 33·72 | 33·82 | 33·44 |
| Hydrogen | 1·98 | 1·98 | 1·82 | 1·87 | 1·93 | 1·87 | 1·89 |

In the following experiments the nitrogen of the nitrococcusic acid was ascertained by burning with oxide of copper in an atmosphere of carbonic acid.

VIII. ·6808 grm. (*b*) dried at 100° C. gave 84 cub. cent. of moist nitrogen at 6°·5 C. and 0·7585 m. barometer corrected.

IX. ·7162 grm. (*c*) dried at 100° C. gave 91·5 cub. cent. of moist nitrogen at 17°·5 C. and 0·7641 m., barometer corrected.

These numbers correspond to the following per-centage quantities:—

| | VIII. | IX. | Mean. |
|---|---|---|---|
| Nitrogen . . | 15·03 | 14·92 | 14·97 |

X. In this experiment the nitrogen was determined according to Bunsen's* method, which consists in burning the substance mixed with oxide of copper in the presence of copper turnings in a hard glass tube. The tube being freed from air by a stream of hydrogen, is then exhausted, sealed hermetically, and placed in an iron mould filled with plaster of Paris; it is then heated to redness and allowed to cool. After the com-

* Liebig's *Annalen*, vol. xxxvii. p. 27.

bustion, the gas is transferred into a graduated jar over mercury and its volume noted; the carbonic acid being absorbed by a potash ball, the volume is again read off. This analysis gave the following numbers:—

| | Vol. | Temp. | Diff. of level. | Barom. |
|---|---|---|---|---|
| Carbonic acid + nitrogen (moist) | 123 | 20°·7 C. | 0m·0640 | 0m·7543 |
| Nitrogen . . . . . | 22·2 | 20°·0 | 0m·1650 | 0m·7529 |

The height of the column of mercury in the eudiometer above the level in the trough and the barometric column are corrected for temperature.

| | | | |
|---|---|---|---|
| Carbonic acid + nitrogen corrected to | 0° C. and barom. | | 1m = 76·84 |
| Nitrogen . . . . . | ... ... | 0° ... | 1m = 12·16 |
| Carbonic acid . . . . . | ... ... | 0° ... | 1m = 64·68 |

$\frac{64{\cdot}68}{12{\cdot}16} = 5{\cdot}32$, which is the ratio of carbon equivalents to one nitrogen equivalent.

The preceding analyses of nitrococcusic acid agree with the following formula, confirmed by the analyses of several of its compounds,

$$C_{16}\,H_5\,N_3\,O_{18},$$

as will be seen on referring to the table.

| | | Theory. | | Experiment. Mean. |
|---|---|---|---|---|
| Carbon . | 16 | 96 | 33·45 | 33·75 |
| Hydrogen | 5 | 5 | 1·74 | 1·91 |
| Nitrogen. | 3 | 42 | 14·63 | 14·97 |
| Oxygen . | 18 | 144 | 50·18 | 49·37 |
| | | 287 | 100·00 | 100·00 |

By analysis VII., in which the precaution was taken of using a very long layer of copper turnings, there was obtained, carbon 33·44, hydrogen 1·89; these numbers agree as closely as possible with the theoretical quantities, as does likewise the nitrogen determination (X.) by Bunsen's method; in this experiment the ratio of carbon equivalents to nitrogen equivalents was found to be as 5·32 to 1, or as 16 equivs. of carbon to 3·007 equivs. of nitrogen; taking analysis VII. as the basis of calculation, it gives 14·67 per cent. of nitrogen, the theoretical number being 14·63.

The acid, as it separates from its aqueous solution, contains water of crystallization, which it loses at 100° C.; four experiments gave the following results:—

| | | | |
|---|---|---|---|
| ·4800 grm. | lost ·0289 grm. | = 6·02 | per cent. |
| ·6613 ... | ... ·0395 ... | = 5·97 | ... |
| ·6586 ... | ... ·0385 ... | = 5·84 | ... |
| ·4804 ... | ... ·0289 ... | = 6·01 | ... |
| | Mean . . | = 5·96 | ... |

This mean corresponds perfectly with the formula

$$C_{16}H_5N_3O_{18}+2Aq,$$

as may be seen by a comparison of the theoretical and experimental numbers.

| | Theory. | | Experiment. Mean. |
|---|---|---|---|
| 1 equiv. dry acid . . . | 287 | 94·10 | 94·04 |
| 2 ... water . . . . | 18 | 5·90 | 5·96 |
| 1 ... crystallized nitrococcusic acid . . | 305 | 100·00 | 100·00 |

*Properties of Nitrococcusic Acid.*—It is of a yellow colour, crystallizing in rhombic plates, and presenting very different aspects, according to the circumstances under which it is crystallized. Its solution stains the skin yellow, it is soluble in cold, but considerably more so in hot water; soluble in alcohol, and very soluble in æther. All its salts dissolve readily in water, and most of them in alcohol; it deflagrates violently on being heated; it dissolves iron and zinc, becoming dark-coloured. It is decomposed by sulphide of ammonium with separation of sulphur and the formation of the ammonia salt of a new acid, which I have not yet examined.

*Compounds of Nitrococcusic Acid.*

*Nitrococcusate of Potash.*—I have prepared this salt by two different methods.

*a.* A solution of nitrococcusic acid in boiling water was accurately saturated with carbonate of potash; by evaporation to a small bulk and cooling, the salt was obtained in small yellow crystals; it was purified by draining and recrystallizing.

*b.* An ætherial solution of the acid was precipitated by the cautious addition of an alcoholic solution of potash; the pale yellow precipitate washed with æther and dried, then dissolved in as small a quantity of cold water as possible, and the solution poured into about five times its bulk of absolute alcohol; after standing some time the salt crystallized in well-formed crystals; it was washed with æther and dried. The ætherial washings being added to the mother-liquor, a further portion was obtained and washed with æther. The latter process is less troublesome than the process *a.*

I. ·5469 grm. (*a*) dried at 100° C. were dissolved in a small quantity of boiling water and decomposed by sulphuric acid; dried in a water-bath, the nitrococcusic acid, removed by æther and the residue ignited, gave ·2606 grm. sulphate of potash.

II. ·4383 grm. (*b*) dried at 132° C. gave ·2103 grm. sulphate of potash.

III. ·6251 grm. (*b*) dried at 100° C. and burnt with chro-

mate of lead, gave ·6064 grm. carbonic acid and ·0662 grm. water.

These numbers give the following per-centage quantities:—

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . | ... | ... | 26·46 |
| Hydrogen . | ... | ... | 1·18 |
| Potash . . | 25·74 | 25·92 | |

corresponding with the formula

$$C_{16}\,H_3\,N_3\,O_{16}+2KO,$$

as may be seen by comparing the theoretical and experimental numbers.

| | | Theory. | | Experiment. Mean. |
|---|---|---|---|---|
| Carbon . | 16 | 96 | 26·45 | 26·46 |
| Hydrogen | 3 | 3 | ·83 | 1·18 |
| Nitrogen . | 3 | 42 | 11·57 | |
| Oxygen . | 16 | 128 | 35·26 | |
| Potash . | 2 | 94 | 25·89 | 25·83 |
| | | 363 | 100·00 | |

I was not successful in preparing a nitrococcusate of potash with one equivalent of fixed base; the method I adopted was saturating a given weight of acid with carbonate of potash, and then adding the same amount of acid to the bibasic potash salt; on washing with æther the greater part of the excess of acid was removed, leaving the bibasic salt behind.

*Nitrococcusate of Ammonia.*—This salt was prepared by passing an excess of dry ammoniacal gas through an ætherial solution of the acid dried in the atmosphere; the solution became turbid, and by standing for a short time deposited the salt in clusters of needles adhering firmly to the sides of the vessel; these were removed, washed with æther, and dried on bibulous paper. It is volatile, and sublimes on being heated, most probably with decomposition.

I. ·6011 grm. of the salt dried *in vacuo* was dissolved in a small quantity of boiling water and decomposed by strong hydrochloric acid, which immediately separated the acid in crystals; the mixture was dried in a water-bath, and the nitrococcusic acid removed by æther, a little bichloride of platinum and alcohol being added to the ætherial washings to precipitate a trace of chloride of ammonium. The residue, precipitated as ammonio-chloride of platinum, gave ·8208 grm. of the double chloride.

II. ·6126 grm. dried *in vacuo* and burnt with oxide of copper, the mixture being made in the combustion-tube, gave ·6525 grm. carbonic acid and ·2191 grm. water.

These numbers correspond with the following per-centage quantities:—

| | I. | II. |
|---|---|---|
| Carbon . . . . . | ... | 29·05 |
| Hydrogen . . . . . | ... | 3·97 |
| Oxide of ammonium . . | 15·91 | |

agreeing closely with the following formula,

$$C_{16}\,H_3\,N_3\,O_{16},\ 2NH_4\,O + HO,$$

as may be seen by a comparison of the theoretical and experimental numbers.

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| Carbon . | 16 | 96 | 29·09 | 29·05 |
| Hydrogen | 12 | 12 | 3·64 | 3·97 |
| Nitrogen . | 5 | 70 | 21·21 | |
| Oxygen . | 19 | 152 | 46·06 | |
| | | 330 | 100·00 | |

Or

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| Acid . . . . . | 1 | 269 | | |
| Water . . . . . | 1 | 9 | | |
| Oxide of ammonium | 2 | 52 | 15·76 | 15·91 |
| | | 330 | | |

*Nitrococcusate of Baryta* was prepared by adding an excess of a solution of baryta to an aqueous solution of nitrococcusic acid, a stream of carbonic acid gas being passed through the solution to separate the excess of baryta. The solution was warmed, filtered and evaporated in a water-bath, and again filtered from a small quantity of carbonate of baryta. The evaporation being continued until a pellicle formed on the surface, the solution on cooling deposited this salt in minute yellow crystals. It is insoluble in alcohol, which precipitates it in the form of a jelly from the aqueous solution.

I. ·6750 grm. of substance dried at 100° C. and decomposed by sulphuric acid, gave ·3602 grm. of sulphate of baryta.

II. ·6439 grm. of nitrococcusate of baryta dried at 100° C. and burnt with chromate of lead, gave ·5185 grm. of carbonic acid and ·0800 grm. of water.

These numbers correspond to the following per-centage quantities:—

| | I. | II. |
|---|---|---|
| Carbon . . . . . | ... | 21·96 |
| Hydrogen . . . . | ... | 1·38 |
| Baryta . . . . . | 35·06 | |

agreeing with the formula $C_{16}H_3N_3O_{16} + 2BaO + 2HO$, as may be seen from the following table:—

| | | Theory. | | Experiment. |
|---|---|---|---|---|
| Carbon | 16 | 96·00 | 21·80 | 21·96 |
| Hydrogen | 5 | 5·00 | 1·14 | 1·38 |
| Nitrogen | 3 | 42·00 | 9·54 | |
| Oxygen | 18 | 144·00 | 32·71 | |
| Baryta | 2 | 153·28 | 34·81 | 35·06 |
| | | 440·28 | 100·00 | |

*Nitrococcusate of Silver.*—I attempted to make this salt by boiling oxide of silver with an aqueous solution of nitrococcusic acid, but there was an evident decomposition of the acid, a large quantity of carbonic acid being evolved; after warming the filtered liquor a brown deposit was formed. On filtering off this brown deposit a silver salt was obtained by evaporation, which yielded on analysis—

| | |
|---|---|
| Carbon | 23·64 |
| Hydrogen | 1·26 |
| Oxide of silver | 38·10 |

per-centage numbers not reconcilable with those of nitrococcusate of silver.

On decomposing a hot solution of this salt with hydrochloric acid a new acid was obtained, perfectly distinct from nitrococcusic acid; it crystallized in long needles; very insoluble in water, but soluble in æther and alcohol. I refrain from giving any further account of this acid until the study is completed.

In order to avoid decomposition the nitrococcusate of silver was prepared without the aid of heat, by dissolving carbonate of silver in a cold aqueous solution of nitrococcusic acid and evaporating the filtered solution *in vacuo* over sulphuric acid. The salt crystallized in long bulky needle-like crystals of a yellow colour; when dried at 100° C. the powdered salt becomes deep orange.

It is soluble in alcohol and water, and is highly explosive when heated; in small quantities it may be decomposed by a progressive heat without any violent action; but on attempting to decompose a quantity amounting to ·45 grm. in a porcelain crucible, heated in an air-bath, the salt exploded with great violence, shattering the copper air-bath and driving fragments of the crucible through the copper; the temperature was noted just before the explosion, the thermometer standing at 200° C.; the silver was therefore determined as chloride.

I. ·4698 grm. of substance (*a*) dried at 100° C. and decomposed by nitric acid and the silver precipitated by the addition of hydrochloric acid, gave ·2675 grm. chloride of silver.

II. ·5085 grm. of substance (*b*) dried at 100° C. gave ·2892 grm. chloride of silver.

III. ·8184 grm. of substance (*a*) dried at 100° C. and burnt with oxide of copper, gave ·5700 grm. carbonic acid and ·0554 grm. water.

Corresponding to the following per-centage quantities:—

| | I. | II. | III. |
|---|---|---|---|
| Carbon . . . . . | ... | ... | 18·99 |
| Hydrogen . . . . | ... | ... | 0·75 |
| Oxide of silver . . . | 46·03 | 45·97 | |

and agreeing closely with the following formula,

$$C_{16}H_3N_3O_{16} + 2AgO,$$

as may be seen by the following table:—

| | | Theory. | | Experiment. Mean. |
|---|---|---|---|---|
| Carbon . . . | 16 | 96 | 19·162 | 18·99 |
| Hydrogen . . | 3 | 3 | ·599 | ·75 |
| Nitrogen . . | 3 | 42 | 8·383 | |
| Oxygen . . . | 16 | 128 | 25·549 | |
| Oxide of silver . | 2 | 232 | 46·307 | 46·00 |
| | | 501 | 100·000 | |

*Nitrococcusate of Copper.*—This was made by dissolving carbonate of copper in nitrococcusic acid and deposited on evaporation in pale apple-green needles. I made no analysis of this salt.

The following is a synoptical table of the analyses of nitrococcusic acid and its compounds:—

| | | | |
|---|---|---|---|
| Hydrate of nitrococcusic acid . | $C_{16}H_3N_3O_{16}$ | | $+2HO$. |
| Hydrate of nitrococcusic acid as crystallized from water | ... | ... | $+2HO+2Aq$. |
| Nitrococcusate of potash . . . | ... | ... | $+2KO$. |
| Nitrococcusate of ammonia . . | ... | ... | $+2NH_4O+Aq$. |
| Nitrococcusate of baryta . . . . | ... | ... | $+2BaO+2Aq$. |
| Nitrococcusate of silver . . . . | ... | ... | $+2AgO$. |

The properties of nitrococcusic acid and its salts exhibit a great analogy with those of a number of acids obtained by the action of nitric acid on organic bodies, more especially nitropicric and styphnic acids, from which it differs by the greater solubility of its salts.

If we assume with many chemists the nitrogen of these

acids to exist in the form of hyponitric acid, the formula of nitrococcusic acid will be represented by

$$C_{16}\left\{\begin{matrix}H_3\\3NO_4\end{matrix}\right\}O_4,\ 2HO.$$

This acid would consequently derive from a non-nitrogenous acid, having the composition expressed by the formula

$$C_{16}\,H_6\,O_4,\ 2HO.$$

When I first began this investigation I imagined that a similar relation might exist between nitrococcusic acid and carminic acid; the analysis of these acids, however, as well as the simultaneous production of a large quantity of oxalic acid in its oxidation, showed that this view was erroneous, and that nitrococcusic acid was derived from carminic acid in a more complex manner. Some attempts were made to produce the non-nitrogenous acid, the coccusic acid, but unsuccessfully.

The experiments of MM. Cahours and Laurent on the oxidation of the oils of anise and of tarragon (*Oleum dracunculi*) have made us acquainted with anisic acid, the composition of which is $C_{16}\,H_8\,O_6$. The formula agrees with the composition of the hypothetical hydrated coccusic acid.

Anisic acid, however, as well as nitranisic acid, being monobasic, it was not probable that the further introduction of the elements of hyponitric acid would convert it into a bibasic one; nevertheless it was my intention to have studied the further action of nitric acid on the acids mentioned, in order to obtain if possible trinitroanisic acid, and to compare this substance with the acid obtained from carminic acid, when an account of some new experiments of M. Cahours came under my notice, of the action of a mixture of concentrated sulphuric and nitric acids on anisic acid, by which he has succeeded in preparing trinitroanisic acid. The experiments of M. Cahours have not yet been published in detail, and from his short account it was not possible to decide on the identity or non-identity of nitrococcusic and trinitroanisic acids. A small specimen of anisic acid at my disposal was treated in the manner described by him; after acting for some time water threw down an acid, from the insolubility of which I conclude that these acids are only isomeric.

### *Investigation of the Mother-liquor from which the Carminic Acid had been separated.*

On evaporating the mother-liquors of carminic acid and separating the lead held in solution by means of hydrosul-

phuric acid, they all gave the following results: on acquiring a syrupy consistence, a white chalky-like matter subsided; this was separated by filtration, and proved to be a new crystalline body. The liquor filtered off from this substance deposited a small quantity more on further concentration, and could only be dried to a soft tenacious mass, partly soluble in alcohol, the rest being soluble in water. From three pounds of cochineal five ounces of this soft matter were obtained, showing that the precipitation by a lead salt had effected the separation of carminic acid from a large quantity of foreign matters. This gelatinous matter appears to be of a complex character, but I have not yet examined it fully.

To purify the chalky-like matter, it was well-washed with cold water and crystallized twice by solution in boiling water and evaporation; it was then dissolved by boiling it in a just sufficient quantity of water; animal charcoal was now added, and the ebullition continued for a few minutes; the solution filtered whilst hot deposited on cooling a mass of silky crystalline tufts, completely filling the liquid, and when collected and dried they aggregated into paper-like masses of a silky aspect. I obtained in three experiments 4 parts of the new body from 1000 of cochineal.

I. ·4918 grm. of substance, preparation (*a*), dried *in vacuo* and burnt with oxide of copper, gave 1·0705 grm. carbonic acid and 0·2838 grm. water.

II. ·5680 grm. of substance (*b*) gave 1·2416 grm. carbonic acid and ·3160 grm. water.

III. ·4700 grm. of substance (*b*) gave 1·0210 grm. carbonic acid and ·2660 grm. water.

For the latter analysis I am indebted to the kindness of Mr. Nicholson.

A qualitative examination having pointed out the presence of nitrogen, it was determined by Varrentrapp and Will's method.

IV. ·5046 grm. of substance (*a*) dried *in vacuo* and burnt with soda-lime, gave ·6131 grm. ammonio-chloride of platinum.

V. ·5076 grm. of substance (*b*) gave ·6239 grm. ammonio-chloride of platinum.

From these numbers the following per-centages are calculated:—

| | I. | II. | III. | IV. | V. |
|---|---|---|---|---|---|
| Carbon . | 59·36 | 59·62 | 59·25 | | |
| Hydrogen | 6·41 | 6·18 | 6·29 | | |
| Nitrogen . | ... | ... | ... | 7·62 | 7·71 |

These per-centages, translated into the most simple expression, lead to the formula, $C_{81}\,H_{11}\,NO_6$ as may be seen from the following table:—

| | | Theory. | | Experiment. Mean. |
|---|---|---|---|---|
| Carbon . . . | 18 | 108 | 59·668 | 59·41 |
| Hydrogen . . | 11 | 11 | 6·077 | 6·29 |
| Nitrogen . . | 1 | 14 | 7·735 | 7·66 |
| Oxygen . . . | 6 | 48 | 26·520 | |
| | | 181 | 100·000 | |

Careful and repeated examinations for sulphur proved the absence of this element as a component of the new white substance. I have been unable to produce a compound to control the proposed formula, though several methods were adopted; amongst others, I attempted to form a lead compound by adding acetate of lead to an ammoniacal solution of the substance; I obtained merely a bulky precipitate, consisting of little else than oxide of lead.

This substance is sparingly soluble in cold water, much more so in boiling water; insoluble in alcohol and æther; soluble in hydrochloric acid, which appears to be driven off by evaporation, leaving the substance in large crystals. In a large quantity of nitric acid it dissolves with a slight evolution of gas; the solution evaporated spontaneously furnishes long crystals, which are in all probability a new acid; if dissolved in a small quantity of nitric acid, the mixture becomes spontaneously heated, violent action takes place, and the product is lost; frequently the substance becomes blackened into charred masses. It is soluble in ammonia, from which it is again recovered by the evaporation of the ammonia. It is soluble in the fixed alkalies, and is precipitated from these solutions by saturating with an acid.

In a short paper, entitled "Valerianic Acid and a new body from Casein," Baron Liebig* describes a new substance obtained by fusing casein with hydrate of potash until an evolution of hydrogen takes place along with ammonia. On saturating with acetic acid the aqueous solution of the fused mass an aggregate of fine needles was produced, which were purified by repeated solution in carbonate of potash and re-precipitation by acetic acid. A preliminary analysis led to the formula $C_{16}\,H_9\,NO_5$, differing from the result I obtained in the analysis of the white substance from cochineal by two carbon, two hydrogen, and one oxygen. The properties of the two bodies being however so analogous, it is extremely probable that they are identical, a presumption I am sup-

* Liebig's *Annalen*, vol. lvii. p. 127.

ported in by a comparison of a specimen kindly furnished me by Dr. Hofmann *; further investigations will clear up this point: in the meantime I refrain from proposing a name, as Liebig † has lately proposed the name Tyrosine for the substance prepared from casein. As the latter body arises evidently from a process of oxidation, and as I had obtained the first crop of crystals from a liquid from which the colouring matter had been precipitated by the basic nitrate of lead, I thought that this body might owe its formation to the action of the nitric acid liberated by the sulphuretted hydrogen; but this supposition proved to be erroneous, for in later experiments in which acetate of lead had been used, the same body, and in exactly the same quantity, was obtained. From this we may assume that this substance is contained ready-formed in the cochineal insect.

My engagements for the present preventing me from continuing these researches, I must defer for a future period their completion, but hope to be enabled to communicate to the Society a second paper. In conclusion I may be allowed to express my thanks to my friend Dr. Hofmann for his valuable instruction in the methods of organic research, and his kind advice during the progress of this investigation.

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## CCVI. *On the Nitrates of Bismuth and Copper.*

*By* Mr. John Hall Gladstone, *of University College.*

IN the *Annales de Chimie* for October 1846 appeared a paper by M. Gerhardt, in which he shows that the subnitrate of copper, in whatever manner prepared, has the composition $NO_5$, 4CuO, 3HO; and that the pale blue crystals of neutral nitrate contain four atoms of water of crystallization instead of three, as had been formerly believed.

Upon the publication of this Professor Graham drew my attention to the subnitrate of bismuth, and expressed his opinion that there might be a similar error in the formula assigned to it; especially when it was considered that the per-centage of oxide of bismuth would be almost the same in either case. Now M. Duflos had long since ascribed to the subnitrate of bismuth, formed by decomposing the nitrate by twenty-four times its weight of water, the formula 4BiO, $NO_5$+3HO, thus coinciding with that of the copper salt as determined by M. Gerhardt. It became desirable therefore that the subnitrate of bismuth formed by heating the neutral

* This specimen had been prepared by Baron Liebig himself.—A. W. H.

† Researches on the Chemistry of Food, p. 16.

nitrate, as well as the neutral nitrate itself, should be re-examined.

The subnitrate under consideration may be easily prepared in a state of purity by dissolving metallic bismuth in strong nitric acid, from which the neutral nitrate crystallizes spontaneously, and by subjecting these crystals to a heat of about 300° F. for some hours. The subnitrate thus produced is a white powder yielding up its acid and water at about 500°.

In order to determine the amount of water, a weighed portion of the salt was heated to redness in a tube of hard glass, and the resulting gases passed over metallic copper for the purpose of decomposing the nitric acid, and the water was collected by a chloride of calcium tube. In the first experiment oxide of lead kept at about 300° F. was employed instead of copper, and was found to retain the whole of the nitric acid.

| | I. | II. | III. | Fresh prep. |
|---|---|---|---|---|
| Substance employed | 18·21 | 22·00 | 13·14 | 23·17 |
| Water produced . | 0·57 | 0·79 | 0·43 | 0·69 |

These numbers give respectively 3·1, 3·6, 3·2 and 3·0 per cent.

An estimation of the nitrogen by the absolute method yielded from 17·82 grs. of substance 2·85 cubic inches of gas, equivalent, after due correction, to 18·49 per cent. of nitric acid.

An estimation of the oxide of bismuth, by simply heating the substance to redness in a platinum crucible, gave from 33·635 grs. of subnitrate 26·65 grs. of metallic oxide, or 79·23 per cent.

These numbers very nearly coincide with those deduced from the formula of Prof. Graham, $HO, NO_5 + 3BiO$.

| | By experiment. | By calculation. |
|---|---|---|
| Oxide of bismuth . . | 79·23 | 79·01 |
| Nitric acid . . . . . | 18·49 | 17·99 |
| Water (aver. of 4 expts.) | 3·22 | 3·00 |
| or Nitrogen . . . . . | 4·81 | 4·66 |

There is more than one subnitrate produced by the action of water, and in all probability the "magistery of bismuth" of pharmacy is a mixture of two or more of these. A single experiment of mine yielded 0·9 per cent. of water.

The analysis of the neutral nitrate is attended with far greater difficulty, since it is impossible to free the substance entirely from adhering acid and water without running considerable risk of efflorescence or decomposition. For the first determination of the amount of water, the crystals were drained, dried between folds of blotting-paper, pounded, left

for a day or two *in vacuo* with sticks of caustic potash, and rubbed in dry calico; for the second, the crystals were merely crushed, and pressed for a few minutes between folds of paper; while for the third they were dried, but not pounded.

The following were the results obtained:—

| | I. | II. | III. |
|---|---|---|---|
| Substance employed | 19·02 | 16·46 | 15·63 |
| Water produced . . | 3·715 | 3·21 | 3·04 |

These numbers give respectively 19·5, 19·5 and 19·4 per cent. of water; a close agreement, when it is considered that the substance employed in the third experiment might not be free from adhering water—a circumstance almost impossible in the first.

A similar uniformity exists in the per-centage of oxide of bismuth obtained in different manners. In the first experiment the crystals were pounded, and pressed for a few minutes between folds of blotting-paper, subsequently heated at 300°, so as to obtain the subnitrate already analysed, and, lastly, all the acid and water expelled by a higher degree of temperature. For the second experiment a fresh preparation of the nitrate was made, and the pounded salt was dried *in vacuo* with sticks of caustic potash. In the third and fourth crystals were employed which had remained three days in paper: efflorescence was just beginning to appear. In the fifth experiment the best-looking crystals were chosen, and the oxide of bismuth determined by precipitation. Hoping to obtain the nitrate of bismuth from a less acid solution, I dissolved some of the salt in very dilute nitric acid, but no crystals could be obtained until the evaporation had been carried almost to dryness, when of course the acid liquor had become very concentrated; the salt however was pounded and dried, and furnished the sixth experiment. For the seventh some metallic bismuth was allowed to remain in nitric acid until the acid was so far exhausted as to have little action upon the metal: the mother-liquor was presently filled with minute crystals, which were dried and subjected to analysis. The following are the results of these several experiments:—

| | I. | II. | III. | IV. | V. | VI. | VII. |
|---|---|---|---|---|---|---|---|
| Subs. used . | 29·19 | 27·01 | 26·27 | 22·02 | 19·95 | 14·33 | 14·89 |
| Subnit. prod. | 17·84 | ... | 16·00 | 13·69 | | | |
| BiO obtained | 13·98 | 12·98 | 12·72 | 10·69 | 9·54 | 6·92 | 7·15 |

These numbers give respectively 47·89, 48·05, 48·42, 48·54, 47·82, 48·29 and 48·02 per cent. of oxide of bismuth. And if we consider the atomic weight of the subnitrate as $\frac{300{\cdot}21}{3}$, *i. e.*

100·07, the weight of a single atom of neutral nitrate calculated from the first, third and fourth experiments, will be 163·7, 164·1 and 161·0.

These results are intermediate between the numbers calculated from the formulæ

| | $BiO, NO_5+3HO$. | $BiO, NO_5+4HO$. |
|---|---|---|
| Oxide of bismuth | 49·39 | 46·76 |
| Nitric acid . . | 33·74 | 31·95 |
| Water . . . . | 16·87 | 21·29 |
| | 100·00 | 100·00 |
| Weight of atom . | 160·07 | 169·07 |

They approximate most closely to the numbers deduced from the formula $2(BiO, NO_5)+7HO$.

| | Average of experiments. | $2(BiO, NO_5)+7HO$. |
|---|---|---|
| Oxide of bismuth . | 48·15 | 48·05 |
| Nitric acid . . . | 32·38 | 32·81 |
| Water . . . . . | 19·47 | 19·14 |
| | 100·00 | 100·00 |

If we employ the equivalent for bismuth adopted by Berzelius and Regnault, the neutral nitrate becomes $Bi_2O_3, 3NO_5$, which would be combined with $10\frac{1}{2}$ equivalents of water. If the, not unusual, proportion of 10 atoms be assigned to it, the salt will be expressed by the formula $Bi_2O_3, 3NO_5+10HO$.

This last view does not correspond so closely as the former with the experimental results, but is not altogether incompatible with them.

| | Average of experiments. | $Bi_2O_3, 3NO_5+10HO$. |
|---|---|---|
| Oxide of bismuth . | 48·15 | 48·49 |
| Nitric acid . . . | 32·38 | 33·11 |
| Water . . . . . | 19·47 | 18·40 |
| | 100·00 | 100·00 |

By adopting the high equivalent for bismuth the subnitrate before analysed would be represented by $HO, NO_5+Bi_2O_3$.

I have entered minutely into the detail of my experiments upon nitrate of bismuth, because M. Heintz has recently given * his concurrence to the formula $3NO_5+Bi_2O_3+9HO$; or, if we express the same in the terms of the other theory, $BiO, NO_5+3HO$: he however found somewhat more than the calculated amount of water, a circumstance he attributes to moisture still adhering to the nitrate itself; yet seeing the salt is efflorescent, I cannot but think that the difficulty of drying it is overrated. M. Freundt † gives the following

* *Annuaire de Chimie*, 1846, Millon et Reiset.

† Chemical Gazette, March 1st, 1844.

as the results of his analyses of nitrate of bismuth prepared in three different manners :—

| | | | |
|---|---|---|---|
| Oxide of bismuth | 49·00 | 49·00 | 48·30 |
| Nitric acid . . | 33·25 | 32·33 | 31·08 |
| Water . . . . | 17·75 | ... | 20·62 |
| | 100·00 | | 100·00 |

These numbers, though they do not coincide well with those deducible from any formula, rather favour my view of the composition of this salt. One principal object of M. Freundt's paper is to show that when crystals of nitrate of bismuth are thrown into pure water, besides the subnitrate precipitate we have some of the original salt kept in solution by the liberated acid. I repeated his experiments, and after separating a subnitrate which crystallized from the filtered solution in beautiful feathers of a silvery lustre as soon as it began to evaporate, I obtained crystals having the usual appearance of nitrate of bismuth: 14·93 grs. yielded 7·10 grs. of oxide, which is equivalent to 47·55 per cent.; thus confirming at once M. Freundt's statement and my former analyses.

It was interesting to observe whether the nitrate of bismuth was thus separated entirely from nitrate of copper in the proportion of water these salts contain, and the nature of their constitution.

### *Nitrates of Copper.*

Upon crystallizing a solution of nitrate of copper at about 60° F. (20° Cent.), I uniformly obtained fine blue prismatic crystals, apparently unmixed with any of the salt, containing 6 atoms of water; a result which may be attributed to my having operated at so high a temperature.

The crystals thus obtained are decidedly deliquescent, and do not effloresce like those analysed by M. Gerhardt, which appear to have contained a portion of the higher hydrate. Hence it is impossible to free this salt absolutely from water by means of blotting-paper, but when placed *in vacuo* the crystals speedily become very brittle, and assume a lustrous appearance. The amount of metallic oxide and water was determined as in the analysis of the bismuth salts, and yielded the following results :—

| | Dried in paper. | | | Dried *in vacuo*. | | |
|---|---|---|---|---|---|---|
| | I. | II. | III. | IV. | V. | VI. |
| Substance used | 36·51 | 19·49 | 7·81 | 22·02 | 12·92 | 9·79 |
| CuO obtained . | 12·02 | 6·31 | 2·53 | 7·31 | 4·32 | 3·24 |

These numbers are equivalent to 32·92, 32·38, 32·4, 32·4, 33·44 and 33·1 per cent. of oxide of copper: mean, 32·77.

| | Dried in paper. | | Dried *in vacuo*. | |
|---|---|---|---|---|
| | I. | II. | III. | IV. |
| Substance employed | 14·70 | 11·75 | 9·58 | 10·04 |
| Water obtained . . | 3·56 | 2·70 | 2·07 | 2·11 |

These numbers are equivalent to 24·2, 22·9, 21·6 and 21·1 per cent. of water: mean 22·45; a result which agrees closely with the numbers calculated from the formula originally assigned to this salt by Professor Graham.

| | Average of experiments. | $CuO, NO_5+3HO$. |
|---|---|---|
| Oxide of copper . | 32·77 | 32·90 |
| Nitric acid . . . | 44·78 | 44·73 |
| Water . . . . | 22·45 | 22·37 |
| | 100·00 | 100·00 |

The analysis of the other hydrate of nitrate of copper made by Mr. Graham, indicating 6 atoms of water, is admitted as correct by M. Gerhardt.

The subnitrate produced by heating the neutral nitrate of copper was also analysed in a similar manner; and the following are the results:—

| | |
|---|---|
| Substance employed . . . | 15·75 grs. |
| Oxide of copper obtained . | 10·39 ... |

Equivalent to 66·0 per cent. of oxide of copper.

| | |
|---|---|
| Substance employed . | 6·81 grs. |
| Water produced . . | 0·76 ... |

This is equivalent to 1·11 per cent. of water; a result which confirms the view taken by M. Gerhardt of the composition of this salt, as will be perceived by the annexed numbers:—

| | By experiment. | $NO_5, 3HO, 4CuO$. |
|---|---|---|
| Oxide of copper . | 66·0 | 66·23 |
| Nitric acid . . . | 22·9 | 22·51 |
| Water . . . . | 11·1 | 11·26 |
| | 100·0 | 100·00 |

Hence it is evident that the true composition of the prismatic crystals of nitrate of copper being $CuO, NO_5+3HO$, while that of nitrate of bismuth is $2(BiO, NO_5)+7HO$, there is no relation between the two salts: and the subnitrates of these metals produced by heating their nitrates being respectively $4CuO, NO_5, 3HO$, and $3BiO, NO_5, HO$, shows that they are also entirely separated in this respect.

The rational formulæ for these two classes of salts to which I am disposed to give a preference, are as follows:—

I. Crystallized nitrate of bismuth . $2(BiO, NO_5)+7HO$
Subnitrate of bismuth . . . . $HO, NO_5+3BiO$.

II. Rhomboidal nitrate of copper $CuO, NO_5+6HO$.
Prismatic nitrate of copper . $CuO, NO_5+3HO$.
Subnitrate of copper . . . $CuO, NO_5+3(CuO, HO)$.

The subnitrate thus appears to be formed by replacing the 3 atoms of water in the prismatic nitrate by 3 atoms of the hydrated oxide of copper.

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## CCVII. *On Crystallography, with a Description of a New Goniometer and Crystallonome. By* H. B. Leeson, *M.D.**

DISCRIMINATIVE chemical researches have not received that assistance from crystallography which might have been reasonably anticipated from the natural distinction of form peculiar to various substances whose atoms are free to assume that symmetrical arrangement which is the natural result of certain attractive and repulsive forces pertaining to them.

Many difficulties have concurred to deter persons from devoting greater attention to this branch of science, and to induce a belief that the advantages to be obtained therefrom are not sufficient to compensate the requisite amount of study and labour.

Greater facility in the practical determination of crystalline forms will, it is believed, result from the use of the instruments herewith submitted to the Society; and it is also hoped that the principles of classification now proposed will obviate many of those difficulties consequent on the want of uniform and simple rules whereby to refer a given crystal to its appropriate class and order.

The introduction of any other system, founded on the three gubernatorial axes of Weiss, might perhaps be deemed superfluous, were it not that neither Weiss himself, nor they who have succeeded him, appear to have realized that simplicity or perfection of which the fundamental principle seems to be susceptible.

By referring to the comparative tables of the systems of different authors accompanying the present paper, it will be apparent, not only that the methods of classification are in many instances imperfect and obscure, but also that the

* The first portion of the above paper was read at a meeting of the Chemical Society held March 2, 1846, when the goniometer was exhibited. The second portion was read at a meeting held May 17, 1847, when the crystallonome, figured in Plate I., was exhibited.

nomenclature adopted is more or less confused and inappropriate. The very *same* denomination is employed as characteristic of classes totally *dissimilar* by different authors. Some of the terms employed have reference simply to the *number* of planes bounding a given polyhedron; and since (as hereafter shown) there are polyhedrons possessing the *same number* of planes *similarly disposed* with respect to the gubernatorial axes *belonging to every class and order*, it is evident that terms, such as those alluded to, are inappropriate as distinctive epithets, and calculated to mislead those who have but slightly attended to the subject.

What M. Le Comte de Bournon so pathetically observes, concerning the difficulties he encountered in classing and arranging the various crystals of carbonate of lime, aptly represents the experience of many others who have endeavoured to determine the true primitive form of a crystal according to the various systems heretofore proposed. M. Le Comte writes*, "Je n'ai point encore oublié le travail très-considérable, ainsi que les difficultés énormes que j'ai eu à vaincre, pour parvenir à rassembler et à classer cette quantité immense de cristaux. Ma mémoire se surchargeoit et se fatiguoit, mes cristaux se mélangeoient, mes notes se troubloient par leur multiplicité, et j'ai bien souvent été obligé de recommencer, pour la dixième ou vingtième fois, un travail de reconnoissance très pénible, et qui me déroboit beaucoup de temps pour fixer de nouveau la place que devoit occuper un crystal."

As some may be disappointed by expecting too much, it is well to observe that it must not be supposed that one substance may be distinguished from *every* other by exactly determining its crystalline form; on the contrary, certain forms appear peculiar to certain classes, and are therefore only distinctive of a substance as belonging to such particular class. By a more correct determination of the primitive forms according to the principles contained in the present paper, the extensive existence of isomorphism in certain classes will be remarkably established. Thus it is believed that all the metals, and electro-positive elements, together with most of the simple binary compounds, crystallize in what will be termed in this paper the Rectangular Equiaxial system. It is also probable that all the other simple substances would be found, if crystallized, to belong to the Rectangular class, although perhaps, as is the case with sulphur, of the Inequiaxial order. In compound substances, the nature of the proximate combining elements will determine the peculiar form. Substances com-

* *Traité Complet de la Chaux Carbonatée et de Arragonite*, tom. iii. p. 1. London, 1808.

pounded of many elements will probably belong to the Oblique classes.

Much assistance may be afforded in analysis from a mere drop of any solution crystallized on a slip of glass and examined under the microscope by the aid of the goniometer hereinafter described, more especially when polarized light is also employed. The present paper will, it is hoped, furnish many data calculated to facilitate the knowledge to be obtained of the composition of bodies from observation of their external configuration, especially when the modifications of the position and length of axes dependent on the presence of a given substance have been more accurately determined.

Before explaining the proposed system, it will be necessary to advert to a few general principles conducive to a full comprehension of the subject.

A crystal may be considered as a polyhedral solid, composed of successive layers of matter deposited around a common centre, in planes parallel to those corresponding to the several intersections of two out of three straight lines (not all in the same plane), bisecting each other in such common centre. Such lines are termed the Gubernatorial axes, being evidently indicative of the amount and directions of certain forces concerned in the aggregation of the atoms.

The electric, magnetic and calorific forces on which the symmetrical arrangement of the atoms of substances is no doubt dependent*, will only be slightly adverted to in the present paper. It is however well to observe that the *position* of the so-called gubernatorial axes may be considered as *exponential of the directions of* the planes in which the *forces*, before alluded to, operate to produce the aggregation of the atoms, whilst their *length* or diameter is *indicative of* the *amount* and distance *of such forces*, as exerted from a common centre.

When the amount of force exerted is the same in all directions, no unequal strain or tension of the particles can exist, and hence crystals belonging to the Rectangular Equiaxial system possess no double refraction. When the amount or direction of the aggregating forces is no longer equable, then (the particles being subjected to unequal pressure in certain directions) double refraction necessarily results. Hence the examination of what are termed the optic axes, which the author believes to be situated in the resulting diagonals of the respective parallelograms of force, will assist in determining

* The evolution of flashes of light by certain substances in the act of crystallization and the alteration of the angles of crystals by the application of heat, as observed by Mitscherlich, as also the alteration of the optic axes by heat, may be cited as confirmatory of this hypothesis.

the position and relative length of the axes of crystallization. In consequence of these axes bisecting each other in a common centre, the forces operating on either side such common centre are necessarily equal and similar, and hence the matter arranged on the opposite sides will be also equal and similar in every perfect crystal, where the natural operation of the aggregating forces has not been interfered with, as hereinafter explained. The reason therefore of that symmetry so apparent in perfect crystals will be readily understood, and why such symmetry is most abundant in those substances whose gubernatorial axes possess the greatest equality of length and inclination.

Another consequence of the existence of a common centre of bisection in the axes is, that any perfect crystal may also be considered as a polyhedral solid bounded by planes corresponding to the segments of a sphere, described around such common centre.

The three gubernatorial axes may be considered as primarily representing the three directions in which the *length*, *breadth* and *thickness* of a crystal are progressively increased by the successive strata of matter, such strata being frequently, although not necessarily, indicated by what is termed the cleavage, the facility of which may be dependent on a certain vibratory or intermittent influence of the attractive forces, producing less coherence of the lamina, and occasionally perhaps, owing to a stratum of gas, dust or heterogeneous matter, producing a temporary suspension of aggregation, as frequently experienced in the deposition of metals by galvanism, which is in fact a similar process.

Whatever be the *external* configuration or planes bounding a given crystal, its *interior* structure is believed to be always conformable to the laws already alluded to. When the external planes are parallel to the three primary planes of deposition, the resulting form corresponds to the Hexahedral Parallelopiped, or, as hereinafter defined, the Primary *Uniaxial* Form.

The preceding observations have more especially applied to those perfect or complete crystalline forms in which the natural growth in each direction has been properly developed. Practically numerous cases will be found, in which the growth of the crystal has been interfered with, increased or prevented in certain directions. In examining and classing crystals of that description, it is most important that such circumstances be properly allowed for*, more especially in determining the normal length of the gubernatorial axes.

* In the method commonly employed for obtaining large crystals, which consists in selecting the best and most perfect single crystals from a weak

Were there but one attractive force concerned in the aggregation of the particles, we might expect to have spherical solids composed of concentric layers around the common centre of attractive influence; the general prevalence however of plane surfaces in crystallization indicates the action of more than one such force, and there are strong grounds for supposing that both electric and magnetic forces (the one always intersecting the plane of the other's action at right angles) are conducive to this result. Whether caloric is also to be considered as another description of force apart from those already mentioned, is open to discussion. Knowing that bodies similarly electrified, or similarly magnetized, repel each other, and if dissimilarly attract, and also that no electric force can exist without a magnetic force also existing in a plane at right angles thereto, there are, it is believed, sufficient elements of attractive and repulsive power to account for the symmetrical arrangement of the particles of crystals.

The actual disposition of the magnetic and electric forces existing in and about a sphere, around the equator of which an electric current has been transmitted, will be seen by referring to the annexed diagram (fig. 1), which may serve to illustrate something of the condition of the atoms of a substance during the process of crystallization.

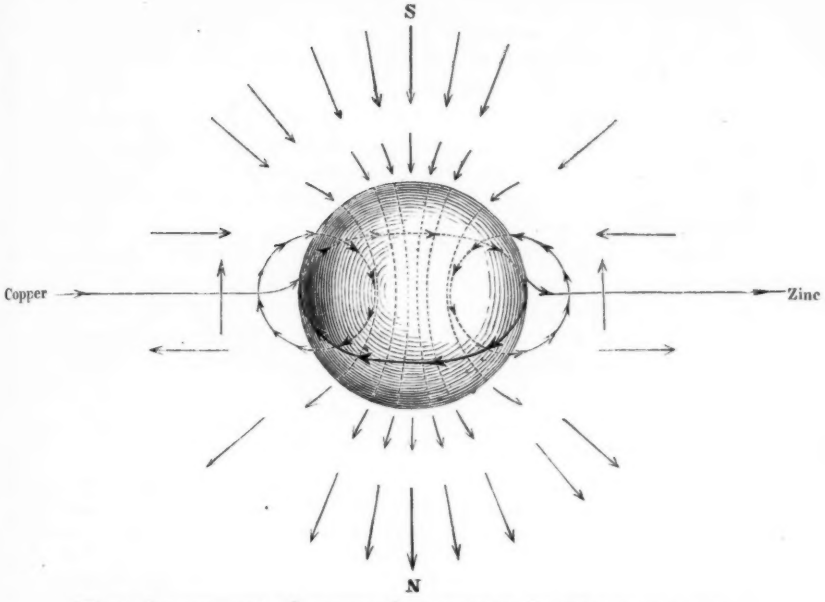
The electric current, as shown by the arrows, is supposed to proceed along a wire attached to the copper extremity of a galvanic battery, and to be led around the farther side of a sphere, returning in front, then round again, and so on, until it finally leaves and proceeds to be attached to the zinc extremity of the galvanic series. The nature of the magnetism consequently developed will be seen by the direction of the little darts, which represent the position assumed by a dipping-needle when presented to the various points of the circumference of the sphere. The barbed extremity of the darts corresponds with the marked end of the needle, or that extremity which usually points to the north.

It will be observed,—

That when the current of electricity rotates, as shown in the diagram, in a right-handed direction, all the portion above the equatorial line will attract the northern extremity of the needle, whilst all that portion below the equator will attract the southern. In other words, the magnetism of the sphere will correspond with that of the earth;

solution of the given salt, placing them at the bottom of a flat vessel containing a saturated solution and turning them frequently; it is well known, that if the crystal is placed on its side it will increase in length, but if placed upright in the vessel on its base it will increase in breadth; the part next the dish receiving no increment, and very often assuming a hollow octahedral form.

Fig. 1.




That the current of magnetism rotates in planes rectangular to the electric current, encircling it on every point of the circumference of the sphere;

That the combined action of all these planes produces a central linear current of magnetism, corresponding with the axis of the electric current;

That coincident with the equator and the plane of the electric current is a neutral line of no magnetic action, *immediately* above and below which the position of the magnetic needle is completely *reversed*;

And lastly, in pursuance of the general laws of magnetic attraction and repulsion, it will be observed that spheres similar to that represented in fig. 1 would (as is apparent in fig. 2) be attractive of each other in the vertical, but repulsive in the equatorial or horizontal direction, unless alternately turned upside down.

Since (as is well known), when the direction of the electric current is reversed, the magnetic polarities are also changed, and it has also been established by experiment that *currents* of electricity are mutually *attractive* if moving in the *same direction*, but *repulsive* if moving *opposite* to each other, it is not improbable that the opposite states of the *positive and negative conditions of matter are dependent on the relative direction of the electric current* rotating around the atoms.

Whether such direction can be ascertained or not, it may suffice for the purpose of illustration to consider those atoms round which the current is right-handed, as in fig. 1, to be the positive elements, whilst those possessing a left-handed current are termed negative*.

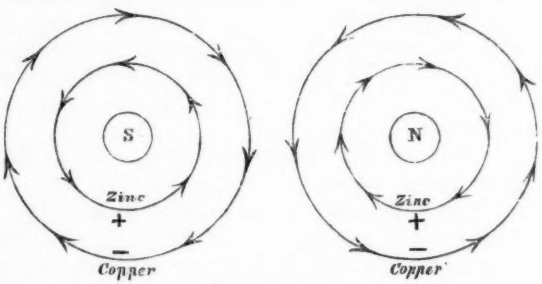
Adopting then the usual signs (+ and −) to denote the positive and negative conditions, and S and N to denote the opposite magnetic polarities, the general disposition of the attractive and repulsive forces in figs. 2, 3, 4 and 5 will be readily understood.

In fig. 2 it is apparent that there would be little tendency to cohesion between the atoms so arranged, the vertical points of magnetic attraction being counteracted by the lateral points of magnetic repulsion, in addition to the naturally repulsive condition of bodies similarly electrified.

Figs. 3 and 4 represent more stable combinations, in which all the magnetic attractions are brought into play to counteract or balance the electric repulsion.

* The general conditions of the argument would not be affected if it be deemed more consonant to fact to term those atoms having a *right-handed* current of electricity *negative*, and those with a *left-handed* current *positive*. If, instead of considering the current of electricity as flowing from the copper to the zinc, it be considered as flowing from the zinc to the copper, or from the positive to the negative element of the galvanic series, then it will only be necessary to reverse the direction of the arrow-heads to show that the current would then be left-handed. In this case not only the magnetic polarities, but also the direction of rotation would exactly correspond to that of the earth itself.

In Ampère's experiment, when concentric cylinders of zinc and copper are suspended in a well of dilute sulphuric acid upon the poles of a magnet, the zinc cylinder or positive element rotates to the left when placed upon the south pole, to the right on the north pole of the magnet; the copper or negative element assuming the converse directions, as seen by referring to the annexed diagram.




If, as is most probable, the rotation of the zinc and copper cylinders be considered as the consequence of a *vis a tergo* or force acting backwards, as in the case of a rocket, then the real direction of the electric currents will be correctly represented in figs. 2, 3, 4, 5 and 7.

Fig. 2.

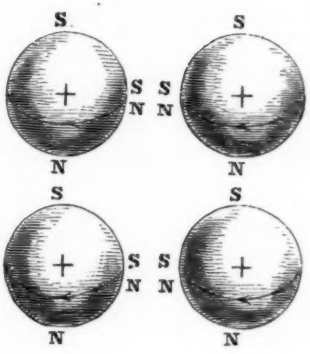


Fig. 3.

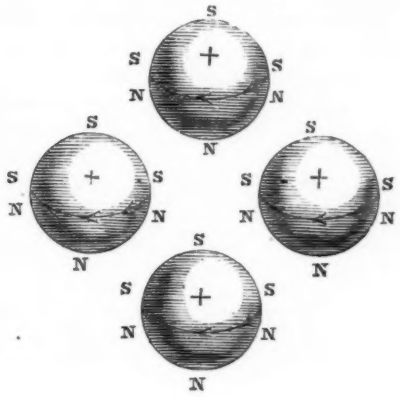


Fig. 4.

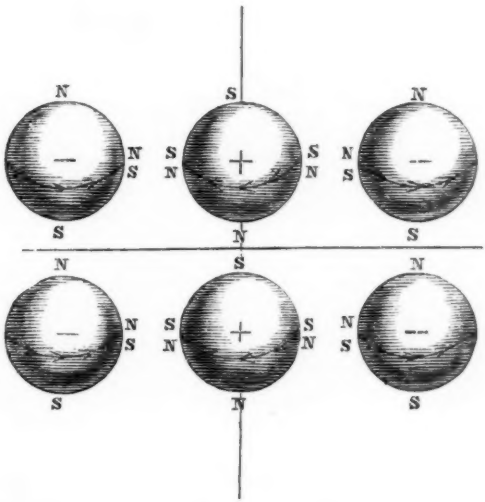


Fig. 4 represents the manner in which oppositely electrified atoms may be supposed to combine; the electric repulsion, if not counterbalanced, being chiefly exerted in a direction tending to separate the strata.

By referring to fig. 4, and more particularly to fig. 5, and considering the directions in which the depth, breadth and thickness would be increased by the addition of other atoms, it will be evident that such directions are represented by the

axes $aa'$ $bb'$ $cc'$, and that the axes $bb'$ $cc'$ are coincident with the equatorial plane of electricity, whilst the axis $aa'$ corresponds to the *vertical* current of magnetic action.

Fig. 5.

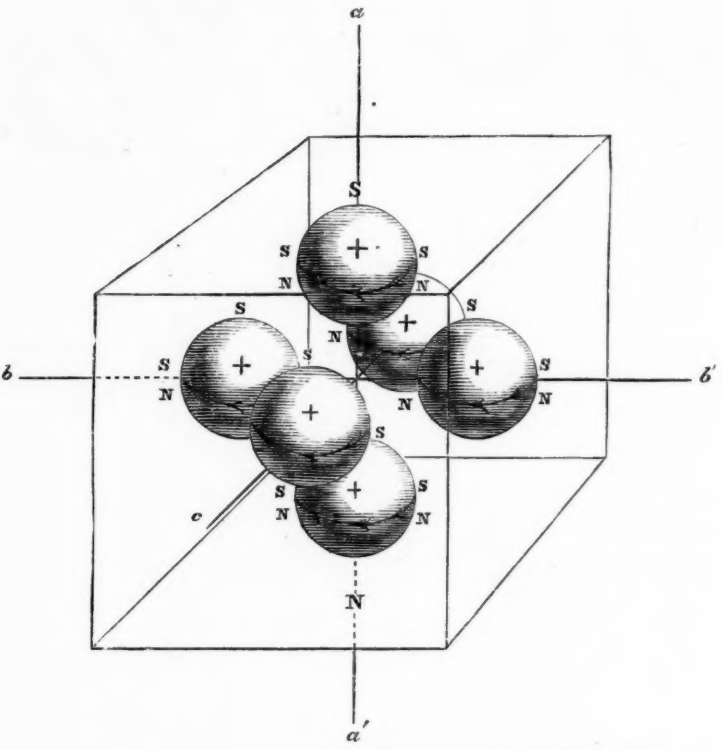
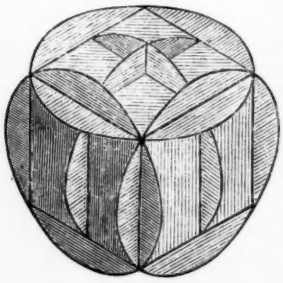



Fig. 6.



The manner in which rectangular planes are produced by the intersection of planes of force rotating around axes rectangular to each other, may be understood by referring to fig. 6. If the axes be inclined, rhombic or rhomboidal planes would result from similar intersections.

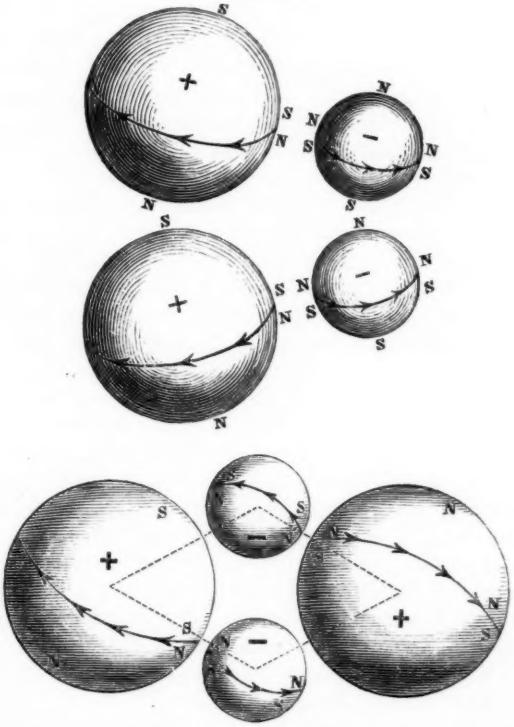
If from any disturbing cause the rotating plane of force assumed an elliptic form, then axes of dissimilar length, corresponding to the major and minor axis of such

ellipse, might be the consequence, as when the mutual repulsions of two similar electric currents are overbalanced by the magnetic attractions.

An illustration of analogous disturbance may be afforded by placing the dissimilar poles of two bar magnets beneath a plate of glass, sprinkling iron or steel filings upon the glass, gradually drawing the magnetic poles apart, and observing the manner in which the curvilinear directions of force assume a more elliptic form as the two foci of magnetic action recede from each other.

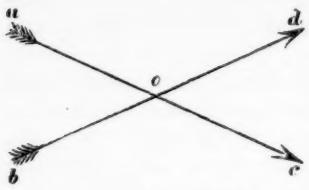
From dissimilar atoms, as in figs. 7, obliquity of the axes *may possibly* result, and it is obvious why such obliquity is

Figs. 7.



likely to be most abundant in substances containing the greatest amount of dissimilar atoms.

If by reason of any arrangement of dissimilar atoms there are two electric currents (*ac*, *bd*) moving in the same direction, and crossing each other (as here represented) in a




given centre (*o*), the portion *ao* will be attracted by the portion *bo*, and *co* by *do*, but the portion *bo* will be repelled by *co*, and *ao* by *do*; thus, a state of unequal tension will be produced, occasioning the existence of optic axes.

The actual coexistence of both attractive and repulsive forces balancing each other is conformable to the generally received opinion, and supposed to be the reason why the atoms of bodies are never in actual contact with each other.

It is probable that the real distinction between simple substances consists in the amount and direction of the electric and magnetic forces rotating around a common centre or point of space, and that matter generally is a mere aggregation of such points or centres of force, which, when free to assume their natural relative positions towards each other, give origin to crystalline or symmetric solids.

When it is said that two substances differ from each other in the relative weight of their respective atoms, as, for instance, when it is stated that the atom of hydrogen weighs 1, and the atom of oxygen weighs 8, the assertion simply enunciates the fact that the attractive influence of the atom of oxygen towards the earth's centre is eight times greater than that of the atom of hydrogen. Whether the difference result from the oxygen possessing eight centres of attractive force, whilst the hydrogen possesses only one, or whether the difference consists in the greater amount of force respectively exerted from only one such centre, still the *distinction* between the two substances, as *possessed of different degrees of attractive force*, cannot be disputed, it being remembered that in this case the comparison is supposed to be made with the same mass, viz. the earth, and at equal distance.

It may therefore be fairly assumed that the attractive forces of the atoms of matter at a given distance are in direct proportion to their atomic weights. The distance which will actually exist between the atoms themselves must depend on the counterbalancing repulsive forces, the precise amount of which has not hitherto been determined.

Whether the repulsive force be *sui generis* and dependent on a peculiar agency termed caloric, or whether it be considered as a mere development of the repulsive forces exhibited between bodies in a similar condition of electric or magnetic excitation, may be subject for discussion. If what is termed specific heat actually represented the amount of

repulsive force exerted between the atoms of bodies at a *given distance*, much important and interesting knowledge would be afforded in studying crystalline arrangement. That the obliquity of the equatorial axes appears to increase in proportion to the specific heat, and that no obliquity exists in the crystals of certain simple substances whose specific heats are in similar proportion to their atomic weights, are circumstances worthy of attention, as also the alterations of the oblique angles and of the optic axes of crystals before adverted to.

As in the Newtonian system the general disposition of the heavenly bodies is the combined result of various attractive masses, each separately tending to modify the system, so in the infinitely smaller space of molecular attraction it is equally necessary to allow for the disturbing influences of extraneous forces in the general phænomena of crystalline arrangement. The prevalence of certain forms of the same substance as peculiar to particular districts is worthy of observation, whether as resulting from the disturbing influences of local magnetic or electric currents, or, as is still more probable, from the combined effect of the disturbing influence of forces belonging to other substances contained in the liquid mass from whence the crystals were themselves deposited. The state of saturation of the liquid itself will also tend to modify the *forms*, by crowding together as it were the centres of attractive and repulsive force.

Having thus briefly suggested some general arguments to demonstrate the actual coexistence of attractive and repulsive forces as inherent in matter; the probable identity of these forces with electricity and magnetism; the dependence of crystalline forms on the lines of direction assumed by the said forces, and the *correspondence of such lines with the so-termed gubernatorial axes*; it might also be demonstrated mathematically, and will be apparent hereafter, that three axes bisecting each other in a common centre, but not all in the same plane, suffice to determine the position and other characters of the planes of any crystalline polyhedron whatever; the axes cut, and the distance from the common centre at which one or more such axes are intersected, being first ascertained.

Assuming then such three gubernatorial axes as the basis of the proposed system, and that $a$, $b$ and $c$ represent such axes, there will necessarily be three distinct planes, corresponding respectively to the intersections of each two of the axes, viz. one corresponding to the intersection of $a$ and $b$, one corresponding to the intersection of $a$ and $c$, and one corresponding to the intersection of $b$ and $c$.

By referring to figs. 8, 10, 12, and 14, which represent the positions of the planes corresponding to the intersection of the axes in examples belonging to the different classes hereinafter proposed, it will be apparent, that whilst the intersection of the axes $aa'$, $bb'$, $cc'$ produce *three* distinct planes, the axes themselves are all contained in any *two* of the planes. Figs. 9, 11, 13, and 15 are more particularly intended to illustrate this

Fig. 8.

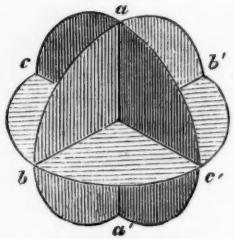



Fig. 10.

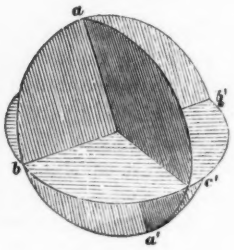



Fig. 12.

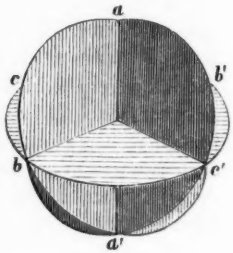



Fig. 9.

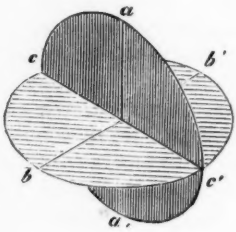



Fig. 11.

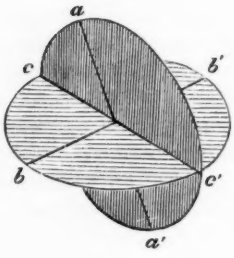



Fig. 13.

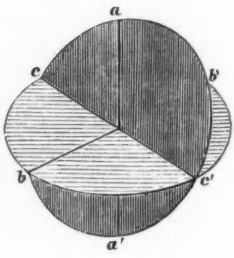



Fig. 14.

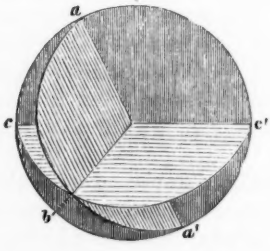
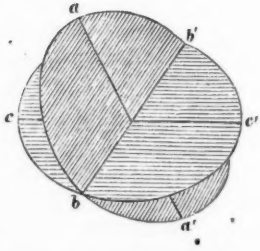



Fig. 15.

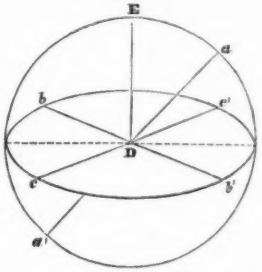



fact, and to show that although any one plane be removed, the two remaining planes still contain the whole of the three axes.

It may also be demonstrated that two planes situated at *right angles* to each other may be so chosen as to contain the whole of the three axes, whatever be their inclination or obliquity to each other. By referring to figs. 8 and 9, it will be apparent that this proposition is true with regard to the Rectangular class, although not equally obvious in the other classes.

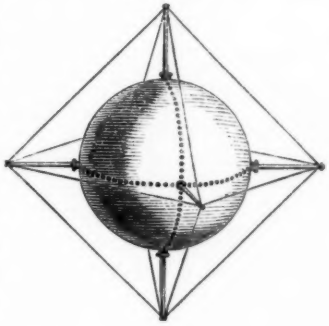
Take any two of the axes *bb' cc'*, fig. 16, and let the plane of their intersection coincide with the horizontal plane *bc b'c'*, of which the common point of bisection D is the centre, then take any third axis, *aa'*, not in the same plane, also bisecting the other axes in D. At D draw D E at right angles to the plane *bc b'c'*, and therefore perpendicular to *bb'* and *cc'*. Then the plane E*aa'*, coinciding with the intersection of ED and *a*D*a'*, will evidently contain the third axis *aa'* and be also rectangular to the horizontal plane *bc b'c'*, containing the other two axes *bb' cc'*.

Fig. 16.




In the system now proposed, the horizontal plane containing the two axes *bb' cc'* will be distinguished as the *Equatorial* plane, whilst the plane E*aa'*, containing the axis *aa'*, will be designated as the *Vertical* plane. The rotation of this vertical rectangular plane, irrespective of the inclination and length of the gubernatorial axes, will be found to govern the character of crystals (as explained hereafter) in a manner which the author believes has not been hitherto observed. The coincidence of these two Rectangular planes with the existence of the two rectangularly situated planes of electric and magnetic force cannot but be remarked. This principle of two rectangularly situated planes containing the whole of the three axes has led to the construction of an instrument for studying the laws and properties of crystalline form, which it is proposed to designate a Crystallonome.

Fig. 17.



The first instrument of this description, contrived by the author and used five years ago for illustration in his lectures delivered at St. Thomas's Hospital, is represented in fig. 17,

and consists simply of a ball made of wood or brass, having two zones or belts of holes pierced at equal distances of 5°, into which holes are screwed wires of equal or different lengths to represent the crystalline axes. These two zones are situated agreeably to the principles already laid down, at right angles to each other. A third zone or belt at right angles to the other two was added in the author's first instrument; but although it affords some facilities in arranging the axes, it is not necessary, and as it tends to complicate the apparatus and increase the trouble of construction, is not recommended.

Since the substance of this paper was first brought before the Chemical Society the author has contrived another instrument, which not only permits a more convenient and universal adjustment of the axes, but also conveys a better illustration of the two rectangularly situated planes.

This instrument is represented in Plate I., which shows the instrument when in use, and also the separate parts of which it is composed. The same letters are employed in designating the parts in all the figures, and the instrument is drawn of a convenient size.

The two rings $d\,d'$, $e\,e'$ represent the circumference of the equatorial plane, and are intended to carry the four wires representing the two equatorial axes $bb'$, $cc'$, which screw into the little overlapping and projecting pieces of brass shown at $f\,f'$, $g$ and $g'$, which are arranged so that the two axes shall move in the same plane.

These two rings are free to move upon each other so that the equatorial axes may be separated any number of degrees, as shown by the graduation upon them. The rings are held in their places by the two plates $h$, $h'$ which fit into the grooves turned in the rings to receive them. These plates are fastened together by three small screws, one of which, $h$, has a projecting head, $i$, to be used to tighten the rings, so that the equatorial axes may be held fast when adjusted.

The two plates $h$, $h'$ are pierced by a longitudinal opening, $k$, through which the plane $m$ carrying the vertical axis $aa'$ is inserted. This plane moves upon and is secured by a central axle, $l\,l'$, fitted into and moving freely between the two plates at $l$ and $l'$. This central axle provides for the depression of the vertical axis any number of degrees from ninety downwards, as shown by the graduation on the vertical plane. The two studs $n$, $n'$ upon this axis are tapped to receive the wires $a$, $a'$ representing the vertical axis. The studs $n$, $n'$ are made of such a length as will occasion the extremities of the wires representing the vertical axis to be equidistant from the common centre with those corresponding to the equatorial axes, sup-

posing wires of equal length to be employed as necessary in the equiaxial system.

This arrangement is also necessary to secure their equal distance from the common centre, when compass-points, of which one is shown at *o*, are substituted (as they may be) for the axial wires *p*, when it is desired to lay down the angles of inclination of the axes, as subsequently explained.

Wires of different appropriate lengths must be used to represent the Binequiaxial and Inequiaxial genera.

The screw at *q* serves to fasten the vertical axis when adjusted. The small groove *r* at the end of each wire is intended to receive and secure the thread, which, when stretched from wire to wire, forms a skeleton model of the Octahedron or *Triaxial* variety of the species to which the instrument is adjusted. The small discs, of which one is shown at *s*, are intended to be fitted by the tube at *t* upon the extremities of the axial wires, and to receive pieces of stiff paper or card-board where it is required to build up the primary parallelopipedal or *Uniaxial* variety of the species. The little pin shown at *u* is to be passed through the centre of the paper or card-board, which is then secured in its place by the nut at *w*. The joint at *x* is for the purpose of adjusting the disc, so that its plane may be parallel with that formed by the intersection of the other two axes.

This instrument is used for the purpose of studying the character and primary forms of any particular Class, Genus or Species, the Class being indicated (as will be explained hereafter) by the inclination or direction of the axial wires, the Genus by their length, and the Species by the position of the vertical plane *m*. The instrument may also be employed with the compass-points for the solution of various problems of spherical trigonometry, more especially those connected with the rotation of the vertical axis.

To use the instrument in examining a crystal, first, screw in the six equiaxial wires and adjust the position of the axes so as to coincide in angular direction with those of the given crystal. When the inclination of the axes has not been previously determined by a goniometer or otherwise, and the examination is simply tentative, a very close approximation to the true position of the axes may be obtained as follows: hold the instrument above the given crystal so that the equatorial plane of the instrument is parallel to that in which the equatorial axes of the crystal are supposed to be situated; then adjust the axial wires so as to be out of winding (as it is termed) with lines passing through the supposed direction of the axes; next adjust the vertical axis in a similar manner,

turning both the instrument and the crystal, so that the planes of intersection of the vertical axis with each of the two equatorial axes may be successively compared and adjusted.

The peculiar arrangement of the parts of the Crystallonome affords that universality of rotation around the common centre necessary to effect the different adjustments or to place the axes in any assignable position. Whether examining a particular crystal or studying the characters of a given Class, Genus or Species, it will be found convenient first to adjust the equatorial axes, then to hold the two rings, into which they screw, tightly with one hand, by pressing them together so as not to shift, whilst with the other hand the vertical axis is placed at its proper elevation and secured by its tightening screw; which being done, it is to be revolved into its true position as regards the other two axes, when by tightening the screw in the equatorial plane the position of all the parts will be finally secured, and axial wires of appropriate lengths may then be substituted if necessary. The instrument being thus adjusted, the Triaxial form may be represented by means of a thread passed from wire to wire, as before explained.

The Uniaxial form may also be built up by means of the discs hereinbefore described. The method of cutting the planes of paper or card-board to their proper shape, consists in ruling two lines bisecting each other at the same angle as that of the pair of axes to which such plane is intended to be parallel, then making the length of each of the two lines coincide with or proportional to that of the axial wires respectively representing such two axes, and ruling through the extremity of each a line parallel to the other axis; thus completing a parallelogram which will correspond to the plane required. Three planes having been thus determined, the opposite three will of course be similar and equal.

This method of representing the Uniaxial form is illustrated in Plates II. III. and IV., wherein, according to the notation already adopted, $aa'$ represents the vertical axis, $bb'$ and $cc'$ the equatorial axes, and $cb\ c'b'$ the equatorial plane or base of the parallelopiped.

The three planes thus drawn upon paper or card-board may be cut out, and being folded at the lines of junction, will represent the primary uniaxial form. It is convenient to leave a little of the waste paper at the margins of the lateral planes, which being folded in and pasted serves to unite them. Of course, if desired, the parallelopiped may be completed by three more planes similarly constructed.

To lay down the inclination of the axes from the crystallonome, substitute the compass-points in place of the axial wires,

and describe a circle exactly equal in diameter to the length of the axes so represented by the compass-points. Then the distance of such points, being marked upon the circumference of the circle; lines drawn therefrom through the centre, will exactly represent the inclination of the axes respectively measured, and their angular distance may at once be determined by the aid of an ordinary protractor. It would be well that the compass-points should be adjusted to a circle of known diameter. Six inches may be recommended as coinciding with the dimensions of the ivory protractors ordinarily sold.

By adjusting the points to the dimensions of a circular protractor, or to a line of chords, the necessity of describing a circle may be altogether avoided. The graduation on the instrument itself gives the angular distance of the equatorial axes and the elevation of the vertical axis, but does not give the angular distance between the vertical and equatorial axes which is most important in studying the new species resulting from the rotation of the vertical plane. This may be ascertained, and the adjustment of the axes accomplished with greater precision by using a circular protractor, or line of chords, in the manner already pointed out, and then the graduation on the instrument itself (which cannot be very minute for want of room) may be altogether dispensed with.

As a simple mode of explaining the author's views, and as a substitute for the instrument described, the paper crystallonome has been contrived as it appears in Plate V. The lower graduated circle represents the equatorial plane with its two axes B and C, one of which (B) is moveable and may be set at any given angular distance from the other (C). The graduated upper semicircle represents one half the vertical plane, and has a moveable index (A) to represent one half the vertical axis. The vertical half plane and axis may be placed at any position upon the equatorial plane, and should be bent up at right angles to it when in use. By applying the points of a compass to the points of the axes when adjusted, and then measuring such distance on the equatorial graduated plane, the angular separation of the vertical with the equatorial axes may be roughly ascertained.

The principles involved in the preceding observations suggest the following data as affording a basis for the proposed system of classification:—

1st. The relative *position* of the gubernatorial *axes* in each of the three planes corresponding to their respective intersections.

2nd. The relative *length* of the *axes*.

3rd. The *position* of the Rectangular plane containing the *vertical axis.*

4th. The relative *disposition of unequal axes.*

5th. The *relation* of the *planes* of any particular form of crystal to the *axes.*

First, as regards the relative position of the gubernatorial axes in each of the three planes corresponding to their respective intersections, figs. 8, 10, 12 and 14, p. 498. There being only three such planes, there can be only the *four* following modes in which the axes can vary with regard to the existence of inclination, that is, obliquity; or of non-inclination, that is, rectangularity to each other, viz. they may be—

1st. Rectangular in all three planes, oblique in none, fig. 8, and Plate II., Class 1.

2nd. Rectangular in two planes, oblique in one, fig. 10, and Plate II., Class 2, fig. 1.

3rd. Rectangular in one plane, oblique in two, fig. 12, and Plate II., Class 2, figs. 2 and 3.

4th. Rectangular in none, oblique in all three, fig. 14, and Plates III. and IV.

Or, which is the same thing, there may exist—

1st. Three rectangular axes.

2nd. Two rectangular axes, one oblique.

3rd. No rectangular axes, all oblique.

The second and third cases in the first arrangement merge into one class, viz. the second of that last proposed. Both cases are in fact comprehended in the one definition of two rectangular axes and one oblique, and differ from each other merely in the relative position of the rectangular plane containing the vertical axis, as will appear presently when treating of its rotation. By referring to Plate II. the Vertical species of the Oblique Rectangular class will illustrate the manner in which two rectangular and one oblique plane coexist, whilst the Bisecting and Intersecting species possess only one rectangular and two oblique planes. In the Bisecting species however of the equiaxial genus both oblique planes are alike, whilst in the Intersecting species they are dissimilar.

In accordance with what has been already stated in the former part of this paper, and again referring to the forms in which various substances are observed to crystallize, it appears that the rectangularity or obliquity of the axes is not only a very permanent but also a striking characteristic of certain classes forming natural groups. Thus the prevalence of three rectangular axes will be noticed in the crystals of simple elements and those of the simpler binary compounds, such as the chlorides, bromides, fluorides, protoxides, sulphurets, &c. By far the largest proportion of the simple

salts, such as the sulphates, phosphates, silicates, &c., belong to the second class and vertical species (Plate II. Class 2, fig. 1) characterized as Rectangular in two planes oblique in one, whilst the more complex compounds, together with the remaining salts, belong generally to the Oblique class. The carbonates appear divided between the Oblique Rectangular and the Oblique class, more generally belonging to the former. Carbonate of lime, one of the hitherto unexplained examples of dimorphism, belongs, as Arragonite, to the Oblique Rectangular class, as Iceland spar to the Oblique*.

When the primary forms are rightly deduced, the true composition more accurately determined, proper allowance made for water of crystallization or accidental impurities, and the production of abnormal forms arising from the action of extraneous forces better understood, the prevalence of natural isomorphous groups distinguished as possessing the same general disposition of the gubernatorial axes will no doubt be greatly extended, and many anomalies, such as dimorphism, explained or removed†.

The foregoing observations will, it is hoped, sufficiently attest the propriety of establishing three distinct classes founded on the data already given, which classes it is proposed to name and define as follows, viz.—

1st. The *Rectangular Class*, in which all the axes are rectangular (Plate II., Class 1).

2nd. The *Oblique Rectangular Class*, in which the vertical axis is oblique, the equatorial axes rectangular (Plate II., Class 2).

3rd. The *Oblique Class*, in which all the axes are oblique (Plates III. and IV.).

The second distinctive datum enumerated has reference to the relative *length* of the three gubernatorial *axes*, which may be—

1st. All of equal length.
2nd. Two equal, the third longer or shorter.
3rd. All three unequal.

* When the primary form of Arragonite is correctly deduced, as it may be from the natural Octohedral or Triaxial form, the angles of the oblique plane (fig. 1, Plate II.) will be found similar to the equatorial angles of Iceland spar, viz. 102° and 78°.

† The dimorphism supposed to exist in the crystalline forms of sulphur disappears when the primary form is properly understood. The crystals obtained by fusion, when examined by the microscope and goniometer subsequently described, evidently belong to the Rectangular class; and on referring the situation of the gubernatorial axes to the corners of the octohedra (pursuant to the rules hereinafter developed), it will be apparent that the crystals naturally occurring also belong to the Rectangular class, and both to what will be presently described as the Inequiaxial genus, the three axes being of unequal lengths.

These distinctions naturally suggest the subdivision of each class into three genera, to be termed respectively—

The 1st. *Equiaxial.*

2nd. *Binequiaxial.*

3rd. *Inequiaxial.*

The proportionate length of the gubernatorial axes is considered a constant characteristic of distinct substances by most who have devoted much attention to crystallography, it is nevertheless a distinction continually masked by that tendency of crystals to grow on the sides most favourably situated, already adverted to in the note, page 489.

As in splitting up a rhomb of calcareous spar various rhombohedrons may be produced of very different proportionate dimensions, so if the relative length of the gubernatorial axes were to be deduced solely from the dimensions of the parallelopipedal forms naturally occurring, the greatest discrepancy would constantly arise even in crystals obtained from the same specimen. This inconvenience is by no means confined to the parallelopipedal form, but applies more or less to other modifications, as will be explained when treating of the laws of elongation.

Attention to the following observations will assist in removing the difficulty referred to. In the Rectangular class, when all the axes are of equal length, the symmetry prevailing on every side and the general tendency towards a spheroidal character, obvious in crystals possessing numerous planes, present peculiarities which cannot well be mistaken.

In the Binequiaxial genus the similarity and regularity of the sides, together with the elongated or flattened form resulting from the greater or less dimensions of the vertical axis, are circumstances easily recognised.

The Inequiaxial genus is distinguished by the similarity and regularity of three opposite aspects; the crystals belonging to this genus possessing as it were back and front, top and bottom, and two sides, each pair consisting of similar and equal opposite sides, but no two pairs being alike.

In the Oblique Rectangular class the prevailing genus is the Binequiaxial.

In the Oblique class the Equiaxial genus is most abundant, and peculiarly characteristic of those substances whose gubernatorial axes in the Bisecting species are similarly and equally inclined. When the axes are of unequal length, the general absence of symmetry will assist in determining the fact, although from examination of those minerals which have been referred by other authors to a doubly oblique system, the existence of any natural crystals belonging to the Oblique Inequiaxial genus now appears very doubtful.

It may be observed generally, that similarity and equality of parts is indicative of similarity and equality in the length and position of the axes around which such parts are severally disposed. Equality of parts is frequently absent, but similarity in the polish, cleavage and general modifications of the forms and edges of the planes of crystals are constant characteristics of the disposition referred to.

The *third* division of the proposed system relates to the *position of* the Rectangular plane containing the *Vertical axis*.

It is a very commonly received opinion, and as such repeated by most authors, that the inclinations of the planes obtained by cleavage are constantly uniform in the same substance. "If (says Phillips in his Introduction to Mineralogy, 3rd edition, 1823, p. xxix.) we cleave a crystal, however large, carbonate of lime for instance, if it be pure and transparent, we shall find by the help of the reflective goniometer (Wollaston's), that the planes of the primary nucleus which will be extracted meet *invariably* under angles of 105°·5 and 74° 55′." From the result of numerous observations made with goniometers of every description, this statement does not appear to be correct in the sense in which it would be naturally apprehended, however constant may be the angles of what is termed the *primitive* nucleus.

Although, by cleaving specimens of carbonate of lime, planes *may* be generally obtained possessing an inclination of 105°·5 and 74°·55, or nearly approximating thereto, still this uniformity will often be confined to the cleavages in *one direction*, whilst in *other directions* very different inclinations may be frequently observed.

The invariability of the measurement in question, even when taken in the proper direction, is by no means so certain as commonly supposed. The following comparison of the observations of various authors will attest the existence of minute differences even in the measurements of the most distinguished observers:—

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Wollaston . . . . . | 105° | 5′ | 0″ | and | 74° | 55′ | 0″ |
| Mitscherlich, at 50° Fahr. . . . | 105 | 3 | 59 | ... | 74 | 56 | 1 |
| Ditto, other observations at 50° F. | 105 | 4 | 45 | ... | 74 | 55 | 15 |
| Dr. H. Kopp* . . . . . | 105 | 15 | 0 | ... | 74 | 45 | 0 |
| Haüy† . . . . . | 104 | 28 | 40 | ... | 75 | 31 | 20 |
| Comte de Bournon‡ . . . . . | 104 | 29 | 0 | ... | 75 | 31 | 0 |

* Brewster, Phil. Mag., April 1841, p. 225.

† *Tableau comparatif des Resultats de Cristallographie.* Paris, 1809, p. 2. See particularly the note, p. 121, in which the Abbe Haüy discusses the measurement of 105° 5′ given by Dr. Wollaston. See also *Traité de Crystallographie*, tome ii. p. 386, Paris, 1822.

‡ *Traité complet de la Chaux Carbonatée.* London, 1808, tom. iii.

It is remarkable, that in regard to the last two measurements of the Abbé Haüy and the Comte de Bournon, Phillips, in the same edition of his work and in the conclusion of the sentence already quoted, speaking of the relative value of the reflecting and common goniometers, falls into the error of supposing that Haüy and Bournon greatly differed. He (Phillips) goes on to observe, "But the angles of this rhomboid, taken by the common goniometer, by perhaps the most skilful hands which ever used it, by the Abbé Haüy and the Comte de Bournon, are given by the first as 104° 28′ 40″ and 75° 31′ 20″, by the second as 101° 32′ and 78° 28′,—a want of agreement in itself sufficient to assure us that the common goniometer is not to be relied on." The error arises from Phillips using the numbers which the Comte de Bournon gives under the column headed "Forme du cristal," and which in fact represent the inclination of the axes, instead of the figures given under the column headed "Angles formés par la rencontre des plans entre eux," which latter column evidently shows that Haüy and Bournon agreed in their measurement, the latter merely disregarding the seconds.

The author's own observations induce him to suppose that crystals may be found in accordance with all these measurements. From other considerations, as well as from actual examination of specimens formerly belonging to Bournon, the author is strongly inclined to suspect, that, after all, Haüy's measurements most nearly represent the true angles of the *primitive* rhombohedron. In deference however to general opinion, and as agreeing with many of his own measurements, the author has adopted 102° and 78° to represent the inclinations of the equatorial axes, whence those of the planes would be 105° 13′ 4″ and 74° 46′ 56″, a result most closely approximating to the observations of Drs. Kopp and Wollaston.

In the page already quoted, Phillips says, "Even the minute crystals, which generally are the most perfect of all, rarely agree in the angles they afford," although taken, it will be observed, by the reflective goniometer, the accuracy of which is so strongly insisted on.

This statement will surprise no one who employs the microscope to examine these minute crystals as well as the small specimens obtained by cleavage, which, although apparently perfect to unassisted vision, will be found constantly possessing a more or less conchoidal fracture when magnified. The difficulty, in fact, of obtaining perfect faces is so great, that the author believes few measurements can be relied on that are not the mean of numerous observations. It will also be apparent presently, as will be seen by referring to the

Tables of the modifications of carbonate of lime, that small as well as much greater differences may actually exist in different species of the same substance in consequence of the rotation of the vertical axis.

The Abbé Haüy observes, in the same work already referred to (*Tableau comparatif*, p. 123), "Une différence plus sensible encore, puisqu'elle va jusqu'à 37′ est celle que présentent les angles primitifs. J'avais négligé, dans le commencement, de les mesurer immédiatement, soit parceque je n'avais aucuns cristaux de la variété primitive qui fussent assez nettement prononcés, soit parceque j'avais remarqué dans les rhomboïdes extrait par la division mécanique dont j'aurais pu me servir, des inégalites qui altéraient le niveau des faces." And again, in his treatise on Crystallography, p. 390, "J'observe d'abord que la mesure donnée par la réflexion outre qu'elle dérive d'un moyen indirect n'a pas un caractère de limite et ne peut être regardée que comme approximative."

Mr. Brookes (deservedly esteemed as one of the most experienced and skilful in the use of the reflective goniometer) observes in his Crystallography, page 444, "The natural planes of crystals are generally too imperfect to give measurements which may be said to agree very nearly with each other; the differences among such as belong to the same species of mineral, amounting frequently to near a *degree*; and the cleavage planes, which generally afford better corresponding results, cannot always be obtained; but if they could, the angles of mutual inclination even of those are *not always alike*, owing probably to an interposition of foreign matter between the laminæ of the crystal and being there unequally dispersed."

Dana, in his Mineralogy*, after alluding to "variations in the angles arising from curvatures and imperfections of surfaces," observes, "Other variations are owing to impurities in the crystal; calcareous spar is one of the most noted instances of this variation; it varies from 105° to 105° 17′. Pure crystals have the constant angle 105° 5′."

The assertion that the alterations in the angles are dependent on impurities in the crystal, is, the author believes, an assumption too hastily adopted; the author possesses a very large and fine specimen of carbonate of lime and iron which strictly coincides in admeasurement with the primary as deduced from the purest forms, whilst, as already stated, many specimens of the purest crystals present differences when cleaved in certain planes.

Instead of 78°, for instance, as the measurement of the acute inclination of the axes, the author has frequently met with fragments measuring little more than 75°, and others

* Second edition, New York and London, 1844.

upwards of 80°, all which apparent anomalies may be explained by the rotation of the rectangular plane containing the vertical axis, to the discovery of which principle the author has been directed by the difficulties adverted to.

In the absence of the crystallonome already described and represented in Plate I., the paper substitute in Plate V. may be used and referred to for the purpose of illustrating the rotation of the vertical axis, the half plane carrying the vertical axis A being first bent up at right angles to the plane containing the equatorial axes B and C. The crystallonome will be adjusted to and represent the Rectangular class by placing the equatorial axes at right angles to each other, that is B at 90°, and also adjusting the vertical axis A to 90°. By rotating the half plane carrying the vertical axis A, it will easily be understood that its rectangularity to the other two axes is not disturbed. In other words, *no* alteration in the relative position of the axes is produced by the rotation of the vertical axis in the *Rectangular class*. Hence this class possesses only *one species*, which will be termed the *Vertical*.

The two equatorial axes remaining as before, let the vertical axis be inclined at *any* angle less than 90° (say 72°), taking care not to disturb the perpendicular position of the half plane containing it. The crystallonome will then be adjusted to the Oblique Rectangular class (Plate II.).

By rotating the vertical plane, it will now be observed that the angles formed by the vertical axis with each of the two equatorial axes, will vary at every point of rotation from 0 to 90° on the equatorial plane. Three principal positions may however be selected.

1st. When the position of the rectangular plane *bisects* or equally divides the right angles formed by the other two equatorial axes, as when placed at 45°.

2ndly. When the rectangular plane *intersects* or *unequally* divides the right angles formed by the equatorial axes, that is, as when placed at any other angle than 45°, say for instance at 30°, or at 10°, or at 52°.

Lastly. When the rotating plane is *vertical* to or exactly stands over either of the other two axes.

The species resulting from these three different positions of the rectangular plane containing the vertical axis, it is proposed to designate and number as follows (see Plate II.) :—

1st. The *Bisecting* species.

2nd. The *Intersecting* species.

3rd. The *Vertical* species.

These are the only three species in the second or Oblique Rectangular class ; but in the third, or Oblique class, five species will result, dependent on the position of the vertical

plane with respect to the *obtuse* or the *acute* angle. There will be for instance (see Plates III. and IV.),

1st. The *Obtuse Bisecting* species. Fig. 1, Plate III.; fig. 11, Plate IV., and figs. 1 and 2, Plate VI.

2nd. The *Obtuse Intersecting*. Figs. 2, 3, 4, Plate III.; fig. 13, Plate IV., and fig. 3, Plate VI.

3rd. The *Vertical* (common to both angles). Fig. 5, Plate III.; figs. 9, 10, Plate IV., and fig. 4, Plate VI.

4th. The *Acute Intersecting*. Figs. 6, 7, Plate III.; fig. 14, Plate IV., and fig. 5, Plate VI.

5th. The *Acute Bisecting*. Fig. 8, Plate III.; fig. 12, Plate IV., and fig. 6, Plate VI.

This division will be better understood by referring to Plate III. and to the two Tables annexed of the rhomboidal modifications of carbonate of lime, the different species of which actually occurring will be illustrated by adjusting the crystallonome to represent the disposition of the axes in a crystal of calcareous spar, for which purpose the half plane containing the vertical axis (A) must be bent up, as before, at right angles to the equatorial plane. Then set the moveable axis (B) to 102°, and the vertical axis (A) as near to 70° 42′ 30″ as the graduation will permit. Next place the vertical plane so as to bisect the obtuse angle 102°, that is at 51°, the crystallonome will then be adjusted so as to represent the position of the axes in the Bisecting Obtuse species of carbonate of lime (fig. 1, Plate III.; also fig. 2, Plate VI.), being the Comte de Bournon's primitive form, allowing for the difference in his measurement, viz. 101° 32′, and that now assumed, viz. 102°.

If the angular distance of the vertical axis (A) from each of the equatorial axes (B and C) be now measured, it will be found to coincide with that of the equatorial axes, viz. 78° and 102°. In other words, all the angles are equal and similar. Knowing this to be the case in the primitive form of carbonate of lime, the inclination of the vertical axis 70° 42′ 30″ has been calculated therefrom.

Again: rotate the vertical plane until it bisects the acute angle (viz. 78°), that is, at 39°, the position of the axes in other respects remaining unaltered; the crystallonome will then be adjusted to represent the Acute Bisecting species (fig. 8, Plate III., and fig. 6, Plate VI.), termed by Haüy the inverse form, it being curious that in this form the relative admeasurements of the angles of the axes and the planes are inverted, as will be apparent by referring to Modification 17 in the annexed Table, taken from Bournon's Treatise. If the angular distance of the axis A from B and C respect-

ively be now measured, it will be found, not 78° as in the Obtuse Bisecting form, but only 75° 7′ 21″, so that the angles in this species are no longer all similar and equal; although in consequence of the vertical plane *bisecting* the acute angle, the triangles formed by A with B and C respectively are isosceles, giving to this form more symmetry than possessed by the Intersecting species.

If the rotating plane be now placed exactly over either of the equatorial axes, the Vertical species (fig. 5, Plate III., and fig. 4, Plate VI.) will be represented. If the angular distances of A from B and C are now observed, A will evidently be 70° 42′ 30″ distant from that axis over which it is placed, whilst from the other axis it will measure 86° 3′ 40″, or 93° 56′ 20″, according to the direction in which it is taken. If the form (fig. 5) be cut out and folded up as before directed, it will be found that two of the sides are upright or perpendicular to the equatorial plane, giving this form that peculiar character which induced Haüy to designate the natural crystals most closely approximating thereto "cuboidal." The form however so termed by Haüy is Bournon's 14th Modification represented in fig. 4, Plate III., which is an Intersecting species, to which the crystallonome may be adjusted by placing the rotating plane at 18° 58′ 38″. This form is erroneously placed by Bournon amongst his acute rhomboids; the fact is, that the Vertical species may be considered either as an acute or as an obtuse rhomb, according to the direction in which it is viewed; this is illustrated by figs. 9 and 10, Plate IV., which in fact make up precisely the same form, as may be observed by copying them on card-board, cutting out and folding up the prism.

The closest natural approximation to the Vertical species (hitherto described) is Bournon's 15th Modification (fig. 6, Plate III.): the Comte dwells particularly on its cuboidal character, and by referring to the Tables it will be seen that the rotating plane is only 5° 4′ 29″ from the exact vertical position.

It is unnecessary to state further how, by referring to the Tables, the crystallonome may be adjusted to the remaining species, and how card-board models may thence be constructed to represent the various parallelopipedal forms.

The rotation of the vertical axis will explain why rhombohedrons of such very different measurements may be obtained from the same substance, and the propriety of constituting distinct species founded on the position of the vertical axis will it is hoped be admitted. The Comte de Bournon and Haüy accounted for these rhombohedral varieties by sup-

posing them to originate in truncatures or decrements of the edges of the primitive form. The fact that the cleavages, and still more frequently the laminæ of crystallization, are nevertheless coincident in many cases with the faces of rhombohedrons differing from the primitive form, seems to have perplexed Haüy *, although easily accounted for by the present theory. There are no doubt some rhombohedral forms in which the cleavages do not accord with the planes of the crystal, such crystals, although apparently Uniaxial, being in fact Biaxial or Triaxial according to the definitions hereinafter explained.

Table of Rhombohedral Modifications of Carbonate of Lime, extracted from the Comte de Bournon's Treatise, 3rd vol.

| Obtuse forms. | | | | | Acute forms. | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Modification. | Form of crystal. | | Angles of planes. | | Modification. | Form of crystal. | | Angles of planes. | |
| No. | Obtuse angle. | Acute angle. | Obtuse angle. | Acute angle. | No. | Acute angle. | Obtuse angle. | Obtuse angle. | Acute angle. |
| | ° ′ | ° ′ | ° ′ | ° ′ | | ° ′ | ° ′ | ° ′ | ° ′ |
| | | | | | 18 | 70 18 | 109 42 | 104 36 | 75 24 |
| Primitive | 101 32 | 78 28 | 104 29 | 75 31 | 17 | 75 31 | 104 29 | 101 32 | 78 28 |
| 7 | 107 3 | 72 57 | 115 42 | 64 18 | 16 | 81 19 | 98 41 | 97 31 | 82 29 |
| 9 | 95 28 | 84 32 | 95 | 85 | 15 | 84 26 | 95 34 | 95 4 | 84 56 |
| | | | | | 14 | 87 42 | 92 18 | 92 12 | 87 48 |

Table of Rhombohedral Modifications of Carbonate of Lime, calculated on the supposition that the Vertical Axis A has a constant elevation of 70° 42′ 30″, and the Equatorial Axes B and C a constant angle of 102°.

| Plate III. | Species. | Distance of Vertical plane. | | Angles of axes. | | Bournon's approximate modification. |
|---|---|---|---|---|---|---|
| Fig. | | From B. | From C. | A and B. | A and C. | |
| | | ° ′ ″ | ° ′ ″ | ° ′ ″ | ° ′ ″ | |
| | OBTUSE. | | | | | |
| 1 | Bisecting ... | 51 0 0 | 51 0 0 | 102 0 0 | 78 0 0 | 102 0 0 | 78 0 0 | Primitive. |
| 2 | Intersecting | 73 14 24 | 28 45 36 | 95 28 0 | 84 32 0 | 106 50 7 | 73 9 53 | 9th. |
| 3 | Ditto ..... | 74 46 13 | 27 13 47 | 94 59 0 | 85 1 0 | 107 3 0 | 72 57 0 | 7th. |
| 4 | Ditto ..... | 83 1 22 | 18 58 38 | 92 18 0 | 87 42 0 | 108 42 18 | 71 47 42 | 14th. |
| 5 | VERTICAL.. | 102 0 0 | 0 0 0 | 86 3 40 | 93 56 20 | 109 17 30 | 70 42 30 | |
| | ACUTE. | | | | | | | |
| 6 | Intersecting | 72 55 31 | 5 4 29 | 84 26 0 | 95 34 0 | 109 12 46 | 70 47 13 | 15th. |
| 7 | Ditto ..... | 62 48 28 | 15 11 32 | 81 19 0 | 98 41 0 | 108 35 32 | 71 24 28 | 16th. |
| 8 | Bisecting ... | 39 0 0 | 39 0 0 | 75 7 21 | 104 52 39 | 104 52 39 | 75 7 21 | 17th. |

The figures in Plate III. are intended to represent the mo-

* *Tableau comparatif des Résultats de la Cristallographie*, 1809, p. 126.

difications of carbonate of lime contained in the last table. Plate IV. is more particularly intended to mark the peculiar characters of the five species *generated* by the *position* of the vertical axis, *without reference to its inclination.*

In concluding this third division of the system, it may be observed generally, that the actual inclination of the vertical axis will be best obtained from the Bisecting species, which species possesses the greatest amount of symmetry. If, as is most probable, other substances follow the analogy of carbonate of lime, it would appear right to choose that bisecting species or parallelopiped as the primitive, the oblique angles of which are all respectively similar and equal. It is evident that the *primitive* equatorial angle will be indicated by cleavage, and by its continual occurrence in some one direction of different species of the same substance. By examining figs. 11 and 12 of the Bisecting species in Plate IV., it will be evident that with the very *same* inclination of *all* the axes producing planes exactly *similar and equal* in both instances, a totally *different* rhombohedron, in one case obtuse, in the other acute, is nevertheless produced, merely by the position of the vertical axis.

It must be remembered, that in all the varieties of rhombohedrons resulting from the rotation of the vertical plane, the inclination of the vertical axis is supposed to be constant; hence the inclination of the edge A (fig. 1, Plate VI.*) taken across the equatorial plane P, which in fact coincides with the inclination of the vertical axis, is the same in all the resulting species. This inclination is what Bournon terms the salient angle, and his having found it the same both in his 1st and 17th Modifications, that is both in the primitive Obtuse and in the Acute Bisecting species, is a strong corroboration of the principle now advanced. If the Acute Bisecting species had been merely an inversion of the *planes* of the Obtuse Bisecting species, as in figs. 11 and 12, Plate IV., then the inclination of the vertical axis, that is of A upon P, would be found to vary. By copying the Bisecting species in Plates III. and IV. upon card-board, and then cutting out and folding them up as before directed, or by copying the form in wood, this fact will be readily perceived.

That the salient angles of the other modifications described in Bournon's Table do not there appear to correspond with that of the primitive form, is easily accounted for by the cir-

* Plate VI. is intended to represent different rhombohedrons of carbonate of lime, and to show the relative position of the plane containing the vertical axis, as also the method of calculating the various angles by means of right-angled spherical triangles.

cumstance that the inclinations were evidently not all taken across the equatorial plane.

The *Fourth* distinction consists in the *relative disposition of unequal axes*, constituting what will be termed *Varieties*.

In the Binequiaxial and Inequiaxial genera, parallelopipeds of apparently different character result from a variation in the relative position of the longer and shorter axes: thus, in the Binequiaxial genus the axes may vary as follows:—

Var. 1. The Equatorial axes may be both equal, and greater than the Vertical axis.
... 2. The Middle axis may be greater than Vertical axis, Transverse equal thereto.
... 3. The Middle axis may be equal to Vertical axis, Transverse greater than same.
... 4. The Middle axis may be equal to Vertical axis, Transverse less.
... 5. The Middle axis may be less than Vertical axis, Transverse equal thereto.
... 6. The Equatorial axes may be both equal, and less than the Vertical axis.

In the Inequiaxial genus the following varieties may occur:

| | Vertical axis. | Middle axis. | Transverse axis. |
|---|---|---|---|
| Var. 1. | Least. | Greatest. | Less. |
| ... 2. | Less. | Greatest. | Least. |
| ... 3. | Least. | Less. | Greatest. |
| ... 4. | Less. | Least. | Greatest. |
| ... 5. | Greatest. | Least. | Less. |
| ... 6. | Greatest. | Less. | Least. |

These modifications will be observed in the synopsis of classification subsequently given. The class and species to which any variety belongs will be more readily observed by taking a section of the parallelopiped, such that its twelve edges shall be all of equal length, and hence corresponding to the equiaxial genus.

The prolonged experience of the author induces him now to believe that comparatively few of these varieties will be found actually occurring in nature, and that the existence of three unequal gubernatorial axes obliquely disposed is of very rare occurrence. In the proposed system of arrangement it does not however appear advisable to omit a niche for any modification which can possibly result from the variation of the gubernatorial axes, reserving to future investigation and a more widely-extended experience to determine what variations are not to be found actually occurring in the domains of nature.

The *Fifth* and last division of the system comprises the *relation* of the *planes* of any particular form of crystal to the *axes*.

It is a very simple but important law, easily demonstrated, and greatly facilitating crystallographic investigations, that *any plane of any crystal whatever must belong to one or other of the three following Forms*, which may be designated and defined as follows:—

1. *Uniaxial*, cutting *one* axis, parallel to two. Examples, Plate IX. figs. 1 and 5. Plate X. fig. 1.

2. *Biaxial*, cutting *two* axes, parallel to one. Exs., Plate IX. figs. 4 and 8, Plate X. fig. 4.

3. *Triaxial*, cutting all *three* axes, parallel to none. Exs., Plate X. figs. 18 and 22.

It is evident that if a plane cuts one or more of the three axes, it must be parallel to the remaining axis or axes, if any; if not, such axis or axes must be cut, which is contrary to the supposition. If a plane did not cut any of the axes, it must be parallel to all of them, which is impossible, inasmuch as they are not all in the same plane.

Crystals possessing planes belonging to *one* only of the above modifications will be denominated *Simple*.

Crystals whose planes are of different descriptions (that is, belonging to more than one of the three principal forms already mentioned) will be considered *Composite*, and must necessarily be comprised in one or other of the four following composite modifications, viz.—

Variety 4. *Biuniaxial*, composed of Uniaxial and Biaxial planes. Exs., Plate X. figs. 2 and 3.

... 5. *Triuniaxial*, composed of Uniaxial and Triaxial planes. Exs., Plate X. figs. 15, 16, 17.

... 6. *Ternobiaxial*, composed of Biaxial and Triaxial planes. Ex., Plate X. figs. 13 and 14.

... 7. *Omniaxial*, composed of Uniaxial, Biaxial and Triaxial planes. Ex., Plate VIII. figs. 17, 18.

In speaking of the axes cut by the several planes, it is not of course intended to imply that such axes are in all cases situated within the confines of the several planes, but only that such are the axes that either are or would be cut by the respective planes, both axes and planes being produced or extended when necessary.

When the axes, cut by the respective planes, preserve their normal or proportionate lengths, such planes, and all others parallel thereto, are denominated *Primary*. See figs. 1, 3 and 8, Plate VII., figs. 1 to 4 and 15 to 18, Plate X.

When any one or more axes is cut by a plane at a distance differing from its normal or proportionate dimensions, such

planes and all parallel thereto are denominated *Secondary* (see fig. 2, Plate VII., figs. 8 to 12, Plate X.; also figs. 20 to 25, Plate VIII.); the distance at which such axis or axes are cut determining of course the inclination of the plane.

It has heretofore been usual to consider certain forms as restricted to a particular class; thus the Octahedron, Dodecahedron, and various other perfect forms represented in Plate X., figs. 1, 4, 7, 12, 13, 18 and 21, also figs. 21 and 24, Plate VIII., have been supposed to occur only in the Rectangular class. This is certainly true if these terms be restricted to the mathematical definition of the respective regular forms; but since analogous forms subsist in every class, it is now proposed to define a *Form* simply as *composed of a given number of planes having a fixed relationship to the gubernatorial axes**.

The definition of form thus enunciated involves in it a fixity of procedure which eminently characterizes the productions of nature, and which when fully comprehended furnishes the true key to the knowledge and elucidation of crystalline configuration.

The peculiar object of the present paper, is to unfold this method of procedure, as deduced from actual and very extensive examination of minerals and crystals, as also, to explain the anomalies and indicate the causes, by which the relationship of crystals to one common bond of union is obscured and shrouded, and thence finally, to discover the true disposition of the gubernatorial axes, as identified with the amount and direction of the aggregating forces dependent on the nature of the constituent atoms.

The mere explanation of the complexities of geometric form by reference to axes arbitrarily chosen, however interesting to the mathematician, affords little satisfaction to the physical observer, whose more especial object is to obtain that clue which connects external form with chemical constitution, and which can alone determine the isomorphism, dimorphism, &c. of different substances.

Since then *the position of the gubernatorial axes in any given form is constant*, if such position be once accurately determined by the examination of a crystal of any given form in one substance, the observer will have no difficulty in assigning their true position to the gubernatorial axes in whatever substance a similar form presents itself. Hence also the correct primary forms may be readily ascertained and

* The author possesses specimens of carbonate of lime, a substance belonging to the oblique system, crystallized in most of these forms, according to the definition now proposed.

modelled, as before explained in reference to Plates II., III. and IV.

To facilitate the knowledge of the character and relationship of the several forms and their respective planes, the author has employed black spots, or in some cases small circles, to indicate the true position of the gubernatorial axes. By observing these, the number of axes cut by any plane may be easily understood. It must however be remembered, and will be hereinafter explained, that in elongated crystals certain axes may be supposed indefinitely multiplied, although each such axis is still parallel to its original position in the non-elongated form, and must only be reckoned once in relation to any particular plane. It is to indicate such supernumerary axes that small circles have been employed in Plate VIII.

In Plate XII. another mode of designating particular planes has been introduced, by placing spots on the plane itself to indicate the number and direction of the axes cut, one dot being used to signify a uniaxial plane, two dots a biaxial, and three dots a triaxial plane.

There are three causes of frequent occurrence in nature whereby the predominant form of many crystals is so much distorted and apparently altered as to be difficult of recognition by the inexperienced observer. The causes thus adverted to are,—First, the *unequal development of particular planes*, originating what will be termed *Imperfect* forms. Secondly, the *obliteration of certain planes* by such unequal development, producing what will be termed *Defective* forms; and thirdly, the *Elongation* of crystals in particular directions.

The particular manner in which these three causes operate, and the laws by which they appear to be regulated, will be more readily explained when the simple Primary Forms have been first described.

The simple *Primary Uniaxial Form* is a *parallelopiped* composed of six planes, each of which cuts one axis at its normal length, and is parallel to the other two axes. Hence this parallelopiped may be either a cube, a right or inclined rhombic or rhomboidal prism, or a rhombohedron, or simple rhomboidal prism, according to the position and length of the axes.

The simple *Primary Biaxial Form* is a Dodecahedron, or solid of twelve planes, each of which cuts two axes at their normal length, and is parallel to the third axis, fig. 4, Plate X., also shown in skeleton, figs. 7, 8, 10, 11, 12, 13, Plate VII., and in what will hereafter be explained as the Uniaxial aspect, figs. 15 and 18, Plate VII., in the Biaxial aspect, figs. 16 and 19, and in the Triaxial aspect, figs. 4 and 8, Plate IX.

The simple *Primary Triaxial Form* is an Octahedron, or solid of eight planes, cutting respectively the whole three axes at their normal lengths, figs. 18, 22 and 23, Plate X.; also figs. 1 and 22, Plate XII., and represented as a solid nucleus in figs. 7, 8 and 10, Plate VII.

The *Uniaxial* form is evidently susceptible of less variation than either the Biaxial or Triaxial modifications, the position of any uniaxial plane being invariably parallel to two axes, so that although its edges or periphery may be varied by the intersection of other planes, the inclination of the plane itself cannot vary; hence there cannot be any secondary uniaxial planes.

In examining holohedral crystals to ascertain which are the uniaxial planes, it must be remembered—

That the axis cut occupies the *centre* of the plane in the simple form, and corresponds to a line central and parallel to four laterally situated planes.

That the two other axes must exist in a line parallel to the plane itself, dividing the crystal into two halves.

That the cleavages most frequently, although not invariably, coincide in direction with the uniaxial planes.

That uniaxial planes, although they may coexist with other planes, cannot alone originate any other than the parallelopipedal or hexahedral form; and hence that the number of such planes can in no case exceed six in any one crystal.

It will be apparent by referring to Plates II., III. and IV., that the six planes of the simple *Uniaxial* form will be (when not interfered with by the coexistence of Biaxial or Triaxial planes)—

In the First Class, all Rectangular.

In the Second Class, Vertical species, four Rectangular, two Rhombic or Rhomboidal; Intersecting and Bisecting species, two Rectangular, four Rhombic or Rhomboidal.

In the Third Class, all Rhombic or Rhomboidal.

Attention to these circumstances will greatly assist in determining the class when examining crystals with the microscope.

The second or *Biaxial* variety of planes will be more readily understood by supposing them to coincide in position with the planes which would be produced by cutting off the *edges* of the simple uniaxial form, a single truncature of every edge producing ultimately a twelve-sided solid or Dodecahedron (see fig. 1, Plate VII., figs. 1 to 8, Plate IX., and figs. 2 to 4, Plate X.). By reference to the figures, it will be seen that if a plane cuts two axes and is parallel to the third, it must in fact be parallel to an edge of the uniaxial form. As the parallelism is to *one* axis only, it is evident that Biaxial planes may have every variety of inclination in one direction,

although constant in one position, viz. that coinciding with the edge of the prism.

Fig. 2, Plate VII. will illustrate this fact, and explain the manner in which the planes of a secondary Biaxial form, the Pentagonal Dodecahedron, may be supposed to originate, as shown figs. 8 to 12, Plate X.

As there are twelve edges to the Uniaxial Parallelopiped, so the simple Primary Biaxial form has twelve planes corresponding to such twelve edges. In some secondary forms, as for example figs. 5 to 7, Plate X., and figs. 9 to 16, Plate IX., this number is doubled, each edge being, as it were, replaced by two planes. In what is termed a Hemihedral form, that is where half the number of planes are suppressed, the number of primary Biaxial planes will be six, simulating the Uniaxial Hexahedron. See fig. 24, Plate XII. If, as in fig. 12, Plate VII., one-half the number of primary planes are replaced by twelve secondary planes, such as shown in figs. 12 and 16, Plate IX., the total number of Biaxial planes will be eighteen.

The third or *Triaxial* variety of planes may have their relationship to the primary Uniaxial form understood by supposing them to originate in a truncature of the solid angles or corners of the parallelopiped, a single truncature of every angle producing ultimately an eight-sided solid or Octahedron, Plate VII. figs. 3, 7 and 8; Plate X. figs. 15 to 18. The octahedron is believed to be invariably a triaxial form: an Octahedron might, it is true, be supposed to originate from a set of biaxial planes, as in Plate VII. figs. 9, 14 and 17, one-third the number of primary Biaxial planes being suppressed. Such a form does not, however, according to the author's experience, occur in nature, the gubernatorial axes in every natural octahedron examined by the author being situated at the meeting of FOUR planes, and *not*, as supposed and marked in the figures, in the middle of two edges of the Octahedron. Octahedral crystals with biaxial planes have not been hitherto observed by the author.

The number of solid angles in the Uniaxial parallelopiped being eight, the number of triaxial planes coexisting in a crystal will be represented by some function of eight. In the simple primary hemihedral form, the tetrahedron, where half the number of planes are supposed to be suppressed by the extraordinary development of the other planes, the number of course is four. In secondary forms each solid angle is generally replaced either by *three* planes, as in Plate X. figs. 19, 20, 21; Plate VIII. figs. 22 to 24; or by *six* planes, as in Plate VIII. figs. 20, 21, making the total number of coexisting triaxial planes in the first case twenty-four, in the second forty-eight.

It is therefore apparent that the *number* of coexisting similar planes will assist in determining the form to which such planes belong.

Returning to the causes whereby the forms of crystals are distorted and obscured, the undue development of particular planes is first to be considered.

In what will be termed *perfect* forms, all the planes are fully and equally developed according to some given law of relationship to the axes governing the particular form.

It is evident, from the examination of natural crystals, that any one or more of the planes belonging to a given form may be unduly developed or augmented, although the inclination of the plane itself is not affected; such unequal development does not disturb the identity of crystalline form according to the definition already given, however much it may alter the general appearance of the crystal. So long as the number and inclination of the several planes continue constant, the form crystallographically considered is not destroyed; such forms however are denominated *imperfect*; and it will be evident that the periphery or bounding outlines of the planes themselves are no longer uniform. As an illustration of what is here intended, Plate XII. may be referred to. Fig. 1 represents the regular Octahedron or *perfect* simple Primary Triaxial Form of the Equiaxial genus, Rectangular Class. Figs. 4, 7, 14 and 12, are the same form with certain planes unduly developed, constituting what it is proposed to designate *imperfect* forms. In the perfect form the gubernatorial axes are placed at the points of the octahedron, and all the planes are triangular and equal. In the imperfect forms, represented in figs. 4 and 7, the more largely developed planes are hexagonal and the rest trapezoids. In figs. 14 and 12, the augmented planes are also hexagonal, the other four planes continuing triangular. In the last two cases it will be observed the axes are situated in the edges of the crystal. In figs. 4 and 7, the upper and lower planes are augmented at the expense of the remaining planes. Fig. 4 occupies the same position as fig. 1, but fig. 7 is supposed to be placed upon one of the lateral trapezoidal planes. Figs. 4 and 7 may be obtained from fig. 1 by slicing or planing off the upper and lower planes; and the author recommends this to be done by those who would wish fully to comprehend the alterations of form thus produced. In figs. 14 and 12, four planes are augmented at the expense of the other four, thus leading to their complete obliteration in fig. 10, and producing what has been termed a *Defective* crystal, which is the second cause of obscured relationship to be next considered.

The undue development of particular planes, if carried to such an extent as to obliterate any number of the planes existing in the perfect form, will still more completely change the character and appearance of the crystal, so much so that the form itself may even simulate one entirely different. Thus, as occurs in carbonate of lime, and as illustrated in fig. 24, Plate XII., the obliteration of the six lateral planes of the primary biaxial form or Dodecahedron by the two opposite sets of three terminal planes may produce a biaxial hexahedron simulating in external appearance an uniaxial parallelopiped. Forms such as this, in which only half the planes of the perfect form remain, are termed hemihedral. The tetrahedron, fig. 10, is a hemihedral form derived from the octahedron, as already explained. By comparing figs. 22 and 23, it will be seen how the greater development of six planes of the oblique octahedron of carbonate of lime obliterating the other two planes produces the very acute hexahedrons observed in that substance, also simulating uniaxial forms.

These defective forms may be generally detected, not only by observing the cleavages peculiar to the given substance, but also from the circumstance that in many crystals of the same substance the obliteration is not quite completed, some traces of the other planes very commonly remaining. In many cases a complete gradation from the perfect to the defective form may be traced. Another circumstance, which may also greatly assist in the discrimination of these from the true uniaxial forms, although advanced with some diffidence by the author, is the very close approximation to 101° 30′, observed as the inclination of the equatorial axes in the crystals of the salts composed of an acid and a base. The haloid salts are, it is believed, generally if not universally rectangular and equiaxial.

The author has not yet met with any substance the gubernatorial axes of which approximated so closely as 60°. Without therefore asserting that such is absolutely the fact, if a parallelopiped more acute than 60° be met with, there is the strongest probability that such form is not uniaxial. Little difficulty practically occurs in selecting the true uniaxial form. By examining other forms of the same substance it will be easy to observe what disposition of the gubernatorial axes prevails in the given substance.

The most frequently occurring defective form is the hemihedral. Fig. 10, Plate XII., is a primary hemihedral form, the tetrahedron derived from the octahedron, fig. 1. Figs. 4 and 5, Plate XI., are examples of secondary hemihedral forms derived as shown in the Plate from fig. 3.

Sometimes defective planes of a primary form are replaced by secondary planes of the same character; such forms will be termed *mixed* to distinguish them from composite forms, as for example, fig. 12, Plate VII., where the two sets of three primary biaxial planes are replaced by two sets of six secondary biaxial planes; sometimes, as in the composite form, fig. 2, Plate XI., they are replaced by planes of a different character, as in this instance by a single triaxial plane, forming the hexagonal prism erroneously considered a primary form. The combined effects of undue development and elongation are particularly illustrated in Plate XII., more especially representing the peculiar modifications thus resulting from the primary triaxial form, and which will be again adverted to in the general synopsis of forms.

In examining crystals, and more particularly in enunciating the laws which govern the *elongation* of crystals constituting the third cause of distortion before referred to, it will be necessary to define *three directions*, in which, and *in which only* (as the author believes), such *elongation*, as distinguished from mere accretion of several crystals, *takes place*.

1. The *Uniaxial direction*; that is in a line coincident with one of the gubernatorial axes. Plate VIII. figs. 1 and 2, represents the Uniaxial elongation of the simple primary Uniaxial form; fig 3, Uniaxial elongation of the simple primary Biaxial form; fig. 4, Uniaxial accretion of the simple primary Triaxial form.

2. The *Biaxial direction*; that is in a line bisecting two opposite edges of the simple primary uniaxial parallelopiped. Plate VIII. fig. 6, Biaxial accretion of Uniaxial form; fig. 8, Biaxial accretion of Biaxial form; fig. 10, Biaxial elongation of Triaxial form.

3. The *Triaxial direction*; that is in a line joining two opposite solid angles of the primary parallelopiped. Plate VIII. fig. 12, Triaxial accretion of Uniaxial form; fig. 14, Triaxial elongation of Biaxial form; fig. 15, Triaxial accretion of Triaxial form.

By referring to Plate VIII. it is evident that elongation can only produce smooth and perfect crystals when the form elongated possesses a perfect zone of planes parallel to the line of elongation, figs. 1, 2, 3, 10 and 14.

In every other case the apparent elongation will be indicated by striated or indented surfaces, presenting in fact a mere accretion of several distinct crystals, although the general contour may simulate a given form. See fig. 4 simulating fig. 5, fig. 6 simulating fig. 7, fig. 8 simulating fig. 9, fig. 12 simulating fig. 14, and fig. 15 simulating fig. 16*.

* It must not be concluded from hence that a striated surface invariably

It is evident therefore that the simple *Uniaxial* form *can only truly elongate in* the *Uniaxial direction*, figs. 1, 2.

That the simple primary *Biaxial* form *can elongate truly in two* directions, viz. the *Uniaxial*, fig. 3, and the *Triaxial*, fig. 14.

That the simple primary *triaxial* form *can truly elongate in only* one direction, viz. the *biaxial*, fig. 10.

That by elongation in the uniaxial direction the simple primary biaxial dodecahedron originates a four-sided prism, fig. 3, terminated by a four-sided pryamid, the lateral planes of the prism having six not four edges, as in fig. 5, which occurs as a terno-biaxial form.

That by elongation in the triaxial direction the same dodecahedron or simple primary biaxial form originates a six-sided prism, fig. 14, terminated by a trihedral summit, one of the commonest forms occurring in nature.

That the uniaxial elongation has in fact for a basis the quadrilateral aspect of the dodecahedron, figs. 15 and 18, Plate VII., distinguished by *four* planes meeting in one point, which point coincides with one of the gubernatorial axes.

There being three uniaxial directions corresponding to the gubernatorial axes, there are of course three such quadrilateral bases to every dodecahedron; or taking the opposite surfaces, six aspects distinguished by the meeting of four planes.

The triaxial elongation of the simple primary Biaxial form has for its basis the hexahedral outline of the triaxial aspect of the dodecahedron, Plate IX. figs. 4 and 8, distinguished by the meeting of *three* planes in one point. It is in one or more of these centres that the optic axes will most frequently be found, the line joining two such opposite points corresponding in fact to the position of the resulting diagonal of the three gubernatorial axes of force before referred to. In what are termed negative crystals the optic axis appears to be situated in the centre of the obtuse angles, whilst in the so-termed positive crystals it occupies the centre of the acute angles. In the Rectangular binequiaxial system the optic axis necessarily coincides with one of the gubernatorial axes, and would not therefore be situated in the triaxial direction.

As there are four triaxial directions, so there will be four of these hexahedral bases of elongation in the primary dodecahedron; or reckoning as before each surface, eight aspects distinguished by the meeting of three planes in one point.

The primary dodecahedron has another hexahedral outline

indicates a simulated form. The aggregation of unequally extended crystals may occasionally produce an irregular surface. The mere accretion or aggregation of crystals must not be confounded with true elongation.

when looked at in the biaxial direction, distinguished by five planes, as in Plate VII. figs. 16 and 19. In this direction elongation cannot take place without producing a striated surface, as illustrated in Plate VIII. fig. 8.

The simple primary biaxial form or primary dodecahedron is the parent of numerous forms occurring in nature; and it is for this reason that its various aspects have been so largely discussed. It is believed that a perfect familiarity with this form will remove many difficulties incident to the study of crystallography. Plate IX. is intended more particularly to illustrate the passage of simple uniaxial forms into the biaxial, and to indicate in what manner the six-sided prisms, so frequently occurring sometimes terminated with three primary planes (figs. 1 to 8) and sometimes with six secondary (figs. 9 to 16), originate. The figures also in Plates VII. to XII., presenting as they do the constant relationships of the primary forms, will be sufficient it is hoped to prevent the necessity of further tedious detail.

The manner in which the general contour of the Dodecahedron varies, according to the relative position of the gubernatorial axes, will be best apprehended by procuring or making models of the various species.

Much information may likewise be obtained by simply sketching the quadrilateral or uniaxial base of the biaxial form or dodecahedron within the outline of the primary uniaxial form. This is done by bisecting the sides of the uniaxial parallelogram, as in figs. 4, 5, 6, 15 and 18, Plate VII., and then joining the points of bisection by four interior lines. The inclinations of these lines represent the inclinations of the *planes* of the dodecahedron; and as this uniaxial base of the biaxial form is likewise the base of the triaxial form, or octahedron, the inclination of the *edges* of the octahedron is equally represented. If this inclination be first determined from either a biaxial or triaxial crystal, the primary uniaxial form may be deduced conversely by first drawing diagonals to the quadrilateral base, and subsequently ruling four lines at the extremities of such diagonals and parallel thereto, as in fig. 6, Plate VII.

The Triaxial form by its elongation in the Biaxial direction originates a four-sided prism, terminated by a *dihedral* summit, figs. 10 and 11, Plate VIII. The Uniaxial base, or aspect of the octahedron, is, as already stated, quadrilateral, and coincides with that of the dodecahedron. The Biaxial basis, which in fact represents the inclination of the planes of the octahedron, and originates the elongated four-sided prism, is also of course quadrilateral.

The Triaxial basis of the octahedron is hexahedral, and by

elongation in such direction a six-sided prism might be simulated, which however would be known by its striation, and also by the peculiar termination of its extremities by one flat and three inclined planes, as represented in fig. 16, Plate VIII.

It may be stated generally that the gubernatorial axes are commonly found at a point formed, or which would be formed by the meeting of four or eight planes, or of a number corresponding to some function of *four*. When the same crystal possesses some points (as in fig. 21, Plate VIII.) where four and others where eight planes meet, the axes will be most frequently situated at the points where the greater number of planes converge.

The optic axes are usually situated in the line joining the opposite points formed by the meeting of *three* or six planes, or by the meeting of a number of planes corresponding to some multiple of *three*.

The constant occurrence of error in marking planes as belonging to the primary form, so prominent in every work on mineralogy, will be remedied by attention to the foregoing laws. The error is the more remarkable, inasmuch as it has curiously conduced to conceal the extensive existence of isomorphism in substances similarly compounded.

As examples of such error, figs. 5, 7, 9, 11 and 13 have been introduced into Plate VIII., erroneously marked as they occur in different works. It must be premised that the letters P and M are commonly employed as indicating certain planes belonging to the primary, that is, to the Uniaxial form. Thus in fig. 5 the planes M, M′ are supposed to be primary, but are in fact Biaxial, and instead of the four-sided prism forming a portion of the Uniaxial Parallelopiped, it is in fact a portion of the quadrilateral-based prism of the dodecahedron. If the planes M, M′ were indented, as in fig. 4, it is evident that the marking would still be erroneous. Fig. 7 represents a very common method incorrectly adopted of obtaining the Primary form as represented by the dotted lines, in which P, M and M are supposed to be portions thereof. When such a form occurs the plane P is however usually Triaxial, whilst the lateral planes are Biaxial, as shown by the spots in fig. 7. If the longer lateral planes are indented, and the crystal such as shown in fig. 6, then and then only would the planes be correctly marked as quoted. The incorrect marking in figs. 9, 11 and 13, will in the same manner be similarly understood and corrected.

Apophyllite, which crystallizes in the elongated Biaxial form, represented in fig. 3, is a common instance of erroneous marking; the lateral planes being Biaxial, and not Primary

or Uniaxial, as commonly supposed*. It is curious that the small lozenge seen by polarized light in the centre of certain crystals is in fact the Primary Uniaxial nucleus. The elongated form of the octahedron, fig. 11, where two of the planes P, P of the four-sided prism produced are erroneously supposed to belong to the Primary form, is another curious instance wherein the similarity of crystallization in the sulphates of baryta and strontia has been overlooked, no one appearing to imagine the common crystals of sulphate of strontia to be in fact elongated octahedrons.

The silicates might also be referred to as commonly occurring in this elongated triaxial form, and by turning the figures thereof, as represented in various works, at right angles to their usual position, the faces of the octahedron will be easily recognised, as for example, fig. 12, Plate XI., being a figure of pyroxene taken at random from Haüy (*Atlas Traité de Minéralogie*, plate 66, fig. 92 dihexaèdre), but with the true primary triaxial form sketched out upon it, by which it will be seen that the plane erroneously marked P by Haüy as belonging to the primary or uniaxial form is in reality biaxial, whilst the faces incorrectly marked M and M are in reality portions of the primary triaxial form or octahedron, that is triaxial not uniaxial planes.

It will be convenient before proceeding further to propose a *notation* adapted to the system herein enunciated.

The capitals X, Y, Z will be employed to designate the gubernatorial axes in general formulæ when their precise character is not determined; unknown quantities will also be represented by the usual algebraic notation $x$, $y$, $z$.

Roman or upright capitals will designate rectangular axes; italic or inclined letters, oblique.

An axis that either is or may be taken as the vertical axis, will be represented by P or *P*.

The equatorial axes will be designated by M or *M*, T or *T*; M or *M* being the symbol of a *middle* axis, that is of one extending from side to side, as, for example, the axis $b$, $b'$ in the vertical species of the oblique rectangular class, Plate II., whilst T or *T* is applied to *transverse* axes passing through from front to back, such as $c\,c'$ in Plate II. In Plates II. and IV. $c\,b\,c'\,b'$ is the equatorial or horizontal plane, $a\,b\,a'\,b'$ the middle plane, and $c\,a'\,c'\,a$ the transverse plane.

The relative length of the axes will be primarily represented

* As a proof of the correctness of this assertion, the author may refer to specimens in his collection of rose apophyllite crystallized both in the *perfect* Simple Primary Biaxial form or Rhombic Dodecahedron, and also in the elongated form. The cleavages also confirm the truth of the position in question.

by the size of the respective capitals, the longest letter of course representing the longest axis.

The vertical axis is in all cases to be considered as the unit of comparison, and figures may be substituted for the equatorial axes corresponding to their respective lengths. Thus, for example, P22 would exactly represent the relationship of the axes in the binequiaxial example of the rectangular class given in Plate II., such form being also less definitely represented by PMM.

The Bisecting species will be represented by placing P or *P* between the letters indicating the equatorial axes. Examples, M P M, M *P* T.

The Intersecting species by placing the symbol of the vertical axis last. Examples, M M P, M T *P*.

The Vertical species by placing it first. Examples, PMM, *P* M T.

In the Oblique class this mark (⌐) placed over P or *P*, will designate the Obtuse species, and (∧) the Acute.

The synopsis of classification hereinafter given will furnish sufficient examples of the various symbols.

Axes which are mutually convertible will be represented by the same letter, it being a matter of indifference which axis is assumed as occupying the position indicated by the letter employed, provided the general form of the crystal is not thereby misrepresented. Thus, in the subjoined synopsis, Class 3, Genus 3, Species 5, Var. 2, since $M\hat{P}T$ and $M\hat{P}T$ would either represent the same form, although looked at in contrary directions, $M\hat{P}M$ is preferred as symbolic thereof.

It will be observed that it is in consequence of such convertibility that the most symmetrical species present the fewest varieties.

Since the precise position of any given plane is determined by the distance at which such plane (produced if necessary) would cut one or more of the gubernatorial axes, such distance will be represented by figures or fractions placed below the axes cut.

In primary forms no figures will of course be necessary, the axes being all cut at their normal length. A line drawn below one or more of the axial symbols will indicate the axes to which the plane is parallel; thus $P\underline{PP}$ will indicate an Uniaxial plane cutting one axis and parallel to two, and $X\underline{YZ}$ will designate the Uniaxial form; in like manner $P\overline{P}\underline{P}$ would represent a plane of the simple primary Biaxial form, $X\,Y\,\underline{Z}$; and P P P a plane of the Triaxial form XYZ.

A composite form will be denoted by the sign + placed between the symbols of its component forms. Thus a ternobiaxial form would be indicated by $(XY\underline{Z})+(XYZ)$.

In general formulæ of particular forms the symbols X, Y, Z may be understood, and the figures indicating the distance at which the axes are cut employed alone. In this case (0) will of course indicate that the planes do not cut the axis to which such cypher belongs, and (1) that an axis is cut at its normal length. Thus, as in Professor Millar's work on crystallography, 001 or 1.0.0 will represent the simple primary Uniaxial form, the planes of which cut one axis, and are parallel to the other two. In like manner 011 or 1.1.0 will represent the simple primary Biaxial dodecahedron, and 1.1.1 the Octahedron or triaxial form.

An *imperfect* form will be distinguished by a caret (∧) placed below the symbol of the perfect form.

A figure or fraction prefixed to the symbol of a form will denote the relative number of planes substituted for each primary plane: thus 3 (X Y Z) denotes that each plane of the primary triaxial form or Octahedron is replaced by three planes, and hence the form possesses twenty-four planes.

A *defective* form will be denoted by a fraction prefixed to the symbol of the perfect form, such fraction indicating the proportion of unobliterated planes: thus $\frac{1}{2}$ (X Y Z) denotes a hemihedral form containing only four, that is, one-half the number of primary octahedral planes.

Elongated forms will be designated by a line drawn *over* one or more of the axial symbols. If *over one, Uniaxial* elongation will be signified; if *over two, Biaxial* elongation; and when *over* all *three* axes, *Triaxial* elongation.

Having thus explained the notation adopted, the reader will obtain a comprehensive view of the system of classification herein proposed by referring to the subjoined synopsis thereof, which will present a classification of all the varieties that can be produced; assuming any given angle as the inclination of the vertical axis in the 2nd and 3rd Class, also assuming in the 3rd Class any constant angle for the equatorial axes.

## Class I. Rectangular.

Both Vertical and Equatorial axes rectangular.

### Genus 1. *Equiaxial.*

#### Species 1. *Vertical.*

PPP.

Genus 2. *Binequiaxial.*

Species 1. *Vertical.*

Variety 1. PMM.

2. PMM.

Genus 3. *Inequiaxial.*

Species 1. *Vertical.*

PPP.

## Class II. Oblique Rectangular.

Vertical axis oblique, Equatorial axes rectangular.

Genus 1. *Equiaxial.*

| Sp. 1. *Bisecting.* | Sp. 2. *Intersecting.* | Sp. 3. *Vertical.* |
|---|---|---|
| M*P*M. | MM*P*. | *P*PM. |

Genus 2. *Binequiaxial.*

| Species 1. | Species 2. | Species 3. |
|---|---|---|
| Var. 1. M*P*M | Var. 1. MM*P* | Var. 1. *P*PM |
| ... 2. M*P*M | ... 2. MT*P* | ... 2. *P*P M |
| ... 3. M*P*M | ... 3. MT*P* | ... 3. *P*P M |
| ... 4. M*P*M | ... 4. MT*P* | ... 4. *P*P M |
| | ... 5. MT*P* | |
| | ... 6. MM*P* | |

Genus 3. *Inequiaxial.*

| Species 1. | Species 2. | Species 3. |
|---|---|---|
| Var. 1. M*P*M | Var. 1. MT*P* | Var. 1. *P*P M |
| ... 2. M*P*M | ... 2. MT*P* | ... 2. *P*P M |
| ... 3. M*P*M | ... 3. MT*P* | ... 3. *P*P M |
| | ... 4. MT*P* | |
| | ... 5. MT*P* | |
| | ... 6. MT*P* | |

## Class III. Oblique.

Both Vertical and Equatorial axes oblique.

### Genus 1. *Equiaxial.*

| | | |
|---|---|---|
| Species 1. | Obtuse Bisecting . . | $P\breve{P}P$ |
| ... 2. | Obtuse Intersecting . | $MT\breve{P}$ |
| ... 3. | Vertical . . . . . | $PMT$ |
| ... 4. | Acute Intersecting . | $MT\hat{P}$ |
| ... 5. | Acute Bisecting . . | $M\hat{P}M$ |

### Genus 2. *Binequiaxial.*

| | Species 1. | Species 2. | Species 3. | Species 4. | Species 5. |
|---|---|---|---|---|---|
| Var. 1. | $M\breve{P}M$ | $MT\breve{P}$ | $PMT$ | $MT\hat{P}$ | $M\hat{P}M$ |
| ... 2. | $M\breve{P}M$ | $M\breve{T}\breve{P}$ | $PM\breve{T}$ | $M\breve{T}\hat{P}$ | $M\hat{P}M$ |
| ... 3. | | $M\breve{T}\breve{P}$ | $PM\breve{T}$ | $M\breve{T}\hat{P}$ | $M\hat{P}M$ |
| ... 4. | | $MT\breve{P}$ | $PMT$ | $MT\hat{P}$ | $M\hat{P}M$ |
| ... 5. | | $M\breve{T}\breve{P}$ | $PM\breve{T}$ | $M\breve{T}\hat{P}$ | |
| ... 6. | | $M\breve{T}\breve{P}$ | $PMT$ | $M\breve{T}\hat{P}$ | |

### Genus 3. *Inequiaxial.*

| | Species 1. | Species 2. | Species 3. | Species 4. | Species 5. |
|---|---|---|---|---|---|
| Var. 1. | $M\breve{P}\breve{M}$ | $MT\breve{P}$ | $PMT$ | $MT\hat{P}$ | $M\hat{P}M$ |
| ... 2. | | $MT\breve{P}$ | $PMT$ | $MT\hat{P}$ | $M\hat{P}M$ |
| ... 3. | | $M\breve{T}\breve{P}$ | $PM\breve{T}$ | $M\breve{T}\hat{P}$ | $M\hat{P}M$ |
| ... 4. | | $M\breve{T}\breve{P}$ | $PM\breve{T}$ | $M\breve{T}\hat{P}$ | |
| ... 5. | | $M\breve{T}\breve{P}$ | $PMT$ | $M\breve{T}\hat{P}$ | |
| ... 6. | | $MT\breve{P}$ | $PMT$ | $MT\hat{P}$ | |

## Comparative Table

Of Nomenclature adopted by different authors, according to their various systems of classification.

### Class I. Rectangular.

#### Genus 1. *Rectangular Equiaxial Genus.*

Type or Uniaxial form a cube.

| Denomination. | Author. | Class. |
|---|---|---|
| Spheroedric. | Weiss. | 1 |
| Regular. | Rose. | 1 |
| Tessular. | Mohs. | 4 |
| Tesseral. | Naumann. | 1 |
| Monometric. | Dana. | 1 |
| Isometric. | Hausmann. | 1 |
| Cubic. | Beudant. | 1 |
| Cubic. | Dufrenoy. | 1 |
| Octahedral. | Miller. | 1 |

#### Genus 2. *Rectangular Binequiaxial Genus.*

Type, Upright Square Prism.

| Denomination. | Author. | Class. |
|---|---|---|
| Bino-single axed. | Weiss. | 2 |
| Two- and one-axed, or Square Octahedral. | Rose. | 2 |
| Pyramidal. | Mohs. | 2 |
| Pyramidal. | Miller. | 2 |
| Tetragonal. | Naumann. | 2 |
| Dimetric. | Dana. | 2 |
| Monodimetric. | Hausmann. | 2 |
| Square Prismatic. | Beudant. | 3 |
| Right Square Prismatic. | Dufrenoy. | 2 |

#### Genus 3. *Rectangular Inequiaxial Genus.*

Type, Upright Rectangular Prism.

| Denomination. | Author. | Class. |
|---|---|---|
| Single-axed Binary. | Weiss. | 3 *a.* |
| One and one-axed, or Rhombic Octahedral. | Rose. | 4 |
| Prismatic, or Orthotype. | Mohs. | 3 |
| Prismatic. | Miller. | 4 |
| Rhombic. | Naumann. | 3 |
| Trimetric. | Dana. | 3 |
| Trimetric. | Hausmann. | 3 |
| Rectangular Prismatic. | Beudant. | 4 |
| Right Rectangular Prismatic. | Dufrenoy. | 3 |

## Class II*. Oblique Rectangular.

### Genus 1, 2 and 3.

### Species 1 and 2.

### Types, Doubly Inclined Square or Rectangular Prisms.

| Denomination. | Author. | Class. |
|---|---|---|
| Diclinoidric. | Naumann. | 6 |

### Genus 1, 2 and 3.

### Species 3.

### Types, Inclined Square or Rectangular Prisms, or Upright Rhombic and Rhomboidal Prisms.

| Denomination. | Author. | Class. |
|---|---|---|
| Single-axed Bino-unitary. | Weiss. | 3 *b*. |
| Two- and one-membered, or Octahedral. | Rose. | 5 |
| Hemiprismatic, or Hemiorthotype | Mohs. | 5 |
| Monoclinoidric. | Naumann. | 5 |
| Monoclinate. | Dana. | 4 |
| Right Rhomboidal Prismatic. | Beudant. | 3 |
| Oblique Rectangular Prismatic. | Beudant. | 4 |
| Derivation from Oblique Rhomboidal Prismatic. | Dufrenoy. | 5 |
| Oblique Prismatic. | Miller. | 5 |

* The obscurity existing in respect to the comparative length of the axes intended by different authors, as well as the want of some precisely correspondent Class, occasions some difficulty in assigning their true position to the analogous classes of different authors. Rose defines his two- and one-membered, or 5th Class, as having "three axes *all unequal*, two cutting each other obliquely and perpendicular to the third;" corresponding therefore to Class 2, Genus 3, Species 3. Dufrenoy's 5th Type is defined as having *three oblique* axes, two of them equal; corresponding therefore, as far as his definition extends, to Class 3, Genus 2. Beudant terms his 3rd Class "Rectangular or Right Rhomboidal Prismatic," thus mixing together Class 1, Genus 3, with Class 2. His 4th Class is Oblique Rectangular or Oblique Rhomboidal Prismatic; thus again mixing together Classes 2 and 3. Judging however from the crystals quoted as examples by the different authors as belonging to this portion of their system, it is believed that the arrangement now given is the best approximation that can be made to a comparative view in default of exact accordance in their Classes.

The Vertical species of Class II. is that to which the greater proportion of the natural salts belong, and as in these salts the Triaxial form is extremely prevalent, Rose's otherwise inexplicable term Octahedral may have arisen therefrom.

Although, in accordance with the present system (in which the Equatorial axes are always supposed to be situated in the horizontal plane), the Types of Species 3 have been termed Inclined Square or Rectangular Prisms, the more usual method of viewing crystals of this form would account for the terms Right Rhombic or Rhomboidal Prisms, commonly employed. In the system proposed, the square or rectangle must be taken as the base of the prism; but, according to the usual method, the rhomb or rhomboid is so considered.

## Class III. Oblique.

### Genus 1.

### Species 1 and 5.

Obtuse and Acute Bisecting Species of Oblique Equiaxial Genus.

Type, a Rhombohedron.

| Denomination. | Author. | Class. |
|---|---|---|
| Terno-single axed. | Weiss. | 4 |
| Three- and one-axed, or Dodecahedral Hexagon. | Rose. | 3 |
| Hexagonal. | Naumann. | 4 |
| Hexagonal. | Dana. | 6 |
| Monotrimetric. | Hausmann. | 3 |
| Rhombohedric. | Mohs. | 1 |
| Rhombohedral. | Beudant. | 2 |
| Rhombohedral. | Dufrenoy. | 4 |
| Rhombohedral. | Miller. | 3 |

### Genus 1.

### Species 2, 3 and 4.

Intersecting, Obtuse Intersecting Acute and Vertical Species of Oblique Equiaxial Genus.

Types, Oblique Rhomboidal Prisms.

These species would probably be placed in the same class with Genus 3 by other authors.

### Genus 2. *Binequiaxial Genus.*

Types, Long, narrow or short Oblique Rhomboidal Prisms.

The species of this genus would also be placed in the same class with those of Genus 3 by other authors, with perhaps the exception of Dufrenoy, already referred to.

### Genus 3. *Inequiaxial Genus.*

Types, Oblique Rhomboidal Prisms.

| Denomination. | Author. | Class. |
|---|---|---|
| Single-axed Unitary. | Weiss. | 3 *c.* |
| One and one-membered. | Rose. | 6 |
| Tetarto-prismatic, or Anorthotype. | Mohs. | 6 |
| Triclinoidric. | Naumann. | 7 |
| Triclinate. | Dana. | 5 |
| Oblique Prismatic, with Oblique-angled Parallelogram base. | Beudant. | 5 |
| Non-symmetrical Oblique Prismatic. | Dufrenoy. | 6 |
| Doubly Oblique Prismatic. | Miller. | 6 |

## Haüy's Table of Crystalline Forms,

extracted from his *Traité de Minéralogie*, tom. i. p. 263, 2nd edition, Paris, 1822; compared with the system now proposed.

### Class I.

Having a common primitive form of similar dimensions.

1. Cube
2. Regular Octahedron
3. Regular Tetrahedron
4. Rhomboidal Dodecahedron

} Class 1. Genus 1. Rectangular Equiaxial.

### Class II.

Having a primitive form of a similar description, but with dimensions peculiar to each.

1. *Rhomboid.*

* Obtuse
** Acute

} Class 3. Genus 1.

2. *Octahedron.*

* Symmetric . . . Class 1. Genus 2.
** Rectangular . . Class 2. Genus 1. Sp. 3.
*** Rhomboidal . . Class 1. Genus 3.
**** Irregular . . . Class 3.

3. *Quadrangular Prism.*

1. Upright Prism.

* Symmetric . . . Class 1. Genus 2.
** Rectangular . . Class 1. Genus 3.
*** Rhomboidal . .
**** Irregular . . .

} Class 2. Genus 1. Sp. 3.

2. Oblique Prism.

* Rectangular . . Class 2. Sp. 1, 2.
** Rhomboidal . .
*** Irregular . . .

} Class 3.

4. *Regular Hexahedral Prism.*

From what has been stated in the former part of this paper, it will be seen that this form is ternobiaxial, having its two terminal planes triaxial and its lateral planes biaxial. It has been erroneously assumed by Haüy and others as a primary form, and as it occurs in every class and genus cannot be re-

ferred to any one in particular. By referring to the list of minerals mentioned by Haüy as examples, it is evident that, according to the principles of classification contained in this paper, they cannot all belong to the same class, although no doubt Class 3, Genus 1, Sp. 1 and 5 of the present system was chiefly intended.

## Synopsis of Forms.

### Simple Uniaxial Forms.

Planes cutting one gubernatorial axis parallel to the other two.

*Uniaxial Form*

$(X\underline{Y}\underline{Z})$ or 1.0.0.

Synonymes: Hexahedron, Parallelopiped, Quadrangular Hexahedral Prism. Number of planes six.

Upright rectangular prisms belong to Class I.

Inclined rectangular prisms to Class II.

Upright rhombic or rhomboidal prisms to Class II.

Inclined rhombic or rhomboidal prisms to Class III.

In Class I. all six planes are rectangular.

In Class II., Species 1 and 2, two planes are rectangular, four rhombic or rhomboidal.

In Class II., Species 3, four planes are rectangular, two rhombic or rhomboidal.

In Class III. all six planes are rhombic or rhomboidal.

*Uniaxially elongated Uniaxial Form*

$(\bar{X}\underline{Y}\underline{Z})$.

By elongation (which can only produce perfect crystals in the uniaxial direction) various parallelopipeds may be produced, which will differ from the normal form, not in regard to the rectangularity or obliquity of the respective planes, but only as to the length of the edges bounding such planes, whereby square planes may become rectangular parallelograms and rhombic planes rhomboidal. The true normal length of the gubernatorial axes being thereby obscured, must be determined by comparing other crystals of the same substance, more especially those occurring in the primary biaxial or triaxial forms.

To determine the species, it will be convenient to assume the edges of the planes all equal, as would be the case in the Equiaxial genus. If slices parallel to the respective sides be

supposed cut off (when necessary) to produce such equality, a parallelopiped will be obtained corresponding to the given species, Genus 1. By referring to the preceding tabular synopsis of classification, it will be noticed that the Equiaxial genus is not subject to variation, and hence presents less difficulty in the determination of the species.

In simple forms the number of terminal planes situated at either extremity of the quadrangular prism will generally distinguish whether it is

| | | | | |
|---|---|---|---|---|
| Uniaxial, | in which case it is terminated by | | | One plane. |
| Biaxial, | ... | ... | ... | Four ... |
| Triaxial, | ... | ... | ... | Two ... |

*Secondary Uniaxial Forms*

None; the condition of parallelism to two axes precluding any such form.

*Simulated Uniaxial Forms.*

Hexahedrons, composed wholly or partly of biaxial and triaxial planes, may occasionally be confounded with the true uniaxial form, but are to be distinguished therefrom by the means described when treating of such Defective forms.

SIMPLE BIAXIAL FORMS.

Planes cutting two gubernatorial axes, parallel to one.

*Biaxial Form*

(X Y $\underline{Z}$) or 1.1.0.

Synonyme: Rhombic or Rhomboidal Dodecahedron. Example, fig. 4, Plate X.

Number of Planes twelve.

In simple non-elongated forms, if the Planes are all Rhombic, the crystal belongs to Class I.

If all equal, to Genus 1.

If in two sets of four and eight equal Planes, to Genus 2.

If in three sets of four equal Planes, to Genus 3.

If the Planes are partly Rhombic, partly Rhomboidal, the crystal will belong to Class II. or III.

The Vertical species, No. 3, Class II., may be distinguished by two sets of two equal and similar Rhombic Planes, together with two sets of four equal and similar Rhomboidal Planes. If such two sets of four equal and similar Rhomboidal

Planes are both alike, so as to form one set of eight, the crystal will belong to Genus 1 or 2.

If the crystal has a zone of six equal and similar Rhomboidal Planes, it will very probably, unless an elongated crystal, belong to Species 1 or 5, Genus 1, Class III.

If the long side of such Rhomboidal Planes be horizontal to the general direction of the three terminal planes at either extremity of the crystal, it will belong to the *obtuse* species No. 1; if perpendicular, to the *acute* species No. 5.

The other peculiarities of the simple Primary biaxial form have already been largely discussed. The knowledge of the *sets* in which the planes occur will be useful in considering the modifications which crystals undergo, the laws of symmetry *requiring that all the planes belonging to any one set should be similarly treated.* Thus, for instance, as is constantly the case, the zone of six equal and similar primary planes above spoken of will be retained, whilst the two sets of three terminal primary planes will be replaced by two sets of six secondary planes, forming the Hexagonal prism terminated by six-sided pyramids (fig. 12, Plate VII.), or by two triaxial planes forming the common, flat-ended, simple *Hexagonal Prism,* erroneously considered a primary form.

*Hemi-biaxial Form*

$$\frac{1}{2}(X\,Y\,\underline{Z}).$$

The Hexahedron already described as simulating the Uniaxial form and occurring in carbonate of lime (Plate XII. fig. 24), termed by Haüy équiaxe. The nail-headed varieties of carbonate of lime are approximations ($X\,\hat{Y}\,\underline{Z}$) to this form, but the planes of the primary form are seldom wholly obliterated, which circumstance, together with the cleavage, renders this form easy of detection.

ELONGATED PRIMARY BIAXIAL FORMS.

*Uniaxially Elongated Biaxial Form*

$$(\overline{X}\,Y\,\underline{Z}).$$

Synonyme: Quadrangular Prism terminated by four-sided Pyramids (Plate VIII. fig. 3).

This form has already been described and referred to as a common form of apophyllite. It also occurs in zircon, stilbite, idocrase and many other substances.

*Triaxially Elongated Biaxial Form*

$$(\overline{X}\,Y\,\underline{Z}).$$

Synonymes: Triaxially elongated Dodecahedron, Hexagonal Prism with trihedral summits (fig. 14, Plate VIII.).

This very commonly occurring form has also been fully treated of in the previous account of elongated crystals.

The simple Flat Hexagonal Prism is a ternobiaxial form, produced by substituting a single triaxial plane in lieu of each trihedral summit. Its formula is

$$\frac{1}{2}(\overline{\overline{X}\,Y\,\underline{Z}}) + \frac{1}{4}(X\,Y\,Z).$$

SECONDARY BIAXIAL FORMS

$$\begin{pmatrix} X & Y & Z \\ x & y & 0 \end{pmatrix}.$$

*Single Secondary Biaxial Form*

$$\begin{pmatrix} X & Y & Z \\ 1 & x & o \end{pmatrix}.$$

Synonymes: Pentagonal Dodecahedron, Hemitetrahexahedron, Hemitetrakishexahedron, bounded by 12 Pentagonal Planes. Ex., figs. 10 and 12, Plate X.

This form consists in the replacement of each face of the parallelopiped by two pentagonal planes joined base to base, and having the gubernatorial axes situated in the centre of the line formed by such union. By some it is considered a hemihedral form, produced by omitting one-half the planes of the double secondary biaxial form next described, and therefore by them termed Hemitetrahexahedron.

| | Distance at which planes cut axes. |
|---|---|
| 1st Form . | 1, 2, 0 |
| 2nd ... . | 1, $\frac{3}{2}$, 0 |
| 3rd ... . | 1, $\frac{4}{3}$, 0 |

This is a common form of iron pyrites, and occurs also in carbonate of lime.

Fig. 13, Plate X. represents an *Icosahedron*; a Ternobiaxial form resulting from a combination of the Pentagonal Dodecahedron with the simple primary Triaxial form. Its formula is $\begin{pmatrix} X & Y & Z \\ 1, & 2, & 0 \end{pmatrix} + (X\,Y\,Z)$. Iron pyrites occasionally crystallizes in this form, as also sulphoarseniet of cobalt.

*Double Biaxial Form*

$$2\begin{pmatrix} X & Y & Z \\ 1 & x & 0 \end{pmatrix}.$$

Synonymes: Tetrahexahedron, Hexatetrahedron, Tetrakishexahedron, Pyramidal Hexahedron, Hexahedral Trigonal Icositetrahedron, bounded by twenty-four Triangular Planes (fig. 7, Pl. X., figs. 1 and 3, Plate XI.).

In this form one axis is cut at its normal length, and the second axis at a prolonged distance, as expressed in the formulæ of naturally occurring examples. The form itself will be easily comprehended by supposing each face of the primary parallelopiped replaced by a four-sided pyramid.

This form is evidently susceptible of much variation as regards the distance at which the second axis is cut: the author is however doubtful of the existence of so many varieties as contained in the subjoined list, which is based upon the observations of other authors.

| | | Distance at which planes cut axes. |
|---|---|---|
| 1st | Form (most common) . . | 1, 2, 0 |
| 2nd | ... (common) . . . . | 1, 3, 0 |
| 3rd | ... . . . . | 1, 4, 0 |
| 4th | ... . . . . | 1, $1\frac{1}{4}$, 0 |
| 5th | ... . . . . | 1, $1\frac{1}{2}$, 0 |
| 6th | ... . . . . | 1, $2\frac{1}{2}$, 0 |
| 7th | ... . . . . | 1, $3\frac{1}{2}$, 0 |

Gold, garnet, diamond and fluor spar frequently crystallize in this form. Some rare specimens of carbonate of lime in the author's possession, crystallized as represented in fig. 1, Plate XI., prove that this form is not restricted to the regular system.

The obtuse bisecting form, fig. 1, is termed by Haüy "Quinoquaternaire," and is evidently the parent of the *Imperfect* form, fig. 7, termed by Haüy "binosenaire." The letters will indicate the corresponding faces, and show that in fig. 7 the planes *a, b, c, d, e, f,* &c. of fig. 1 are more largely developed, tending to the obliteration of the central zone of faces *k, g, h, l, m, i,* &c.

The contrary larger development of the central zone of planes tending to the obliteration of the terminal planes *a, b, c, d, e, f,* &c., is exhibited in fig. 2, copied from Bournon's *Traité de chaux carbonatée,* plate 19, fig. 311. Fig. 6 represents a similar imperfect form of red silver (argent antimoniée sulfuré), copied from Haüy, and by him termed "apo-

phane." This last appears to be derived from the acute bisecting species, fig. 3, the skeleton lines of which represent the manner in which this form is converted into the defective forms next described.

### Defective Secondary Biaxial Forms.

*Hemihedral Double Biaxial Form*

$$\frac{1}{2}\left(2\binom{X\,Y\,Z}{1\;\;x\;\;0}\right).$$

Synonymes: Double six-sided Pyramid, Isosceles or Scalene Triangular Dodecahedron, Bipyramidal Dodecahedron, bounded by twelve Triangular Planes.

This form is produced, as already sufficiently explained, by the entire obliteration of one-half of the planes of the double secondary biaxial form last described. When the central zone of planes is obliterated by the greater development of the terminal planes, the resulting form is the Isosceles triangular Dodecahedron, fig. 4, Plate XI.; when, on the contrary, the terminal planes are obliterated by the central zone, the Scalene triangular Dodecahedron, fig. 5, is produced.

By observing the coincidence of the dotted lines in figs. 4 and 5, Plate XI. with the edges of the primary uniaxial form, and by studying fig. 3 in the same Plate, as also the figs. 9 to 16, Plate IX., figs. 1 to 7, Plate X., and figs. 11 and 12, Plate VII., it will be apparent that in the isosceles triangular dodecahedron, fig. 4, Plate XI., the *alternate edges of the pyramid correspond to the edges of the primary uniaxial form*, whilst in the scalene triangular dodecahedron, fig. 5, the *bases of the pyramids correspond to edges of the primary uniaxial form.*

Triaxial triangular dodecahedrons resulting in a similar manner from the secondary treble triaxial form, fig. 10, Plate XI., may simulate the biaxial forms just described; the difference however between the two may be traced in the inclination of their planes.

The *acute* triangular dodecahedrons when biaxial are usually scalene, when triaxial isosceles. In this, as in other cases, a series of imperfect forms passing more or less gradually from the perfect to the defective form, will generally occur to establish the connection. Fig. 8, Plate XI. shows the method in which others have supposed this form to originate, but no triuniaxially-formed crystal has been observed by the author justifying such supposition.

This form is generally supposed to occur only in the ob-

lique system, the triangular dodecahedrons of carbonate of lime being familiar examples; specimens however of sulphuret and oxide of copper thus crystallized may be quoted as belonging to the regular system.

*Mixed Biaxial Form*

$$\frac{1}{2}(\mathrm{X\,Y\,\underline{Z}}) + \frac{1}{2}\left(2\begin{pmatrix}\mathrm{X\,Y\,Z}\\ 1\ x\ 0\end{pmatrix}\right).$$

Synonymes: Hexagonal Prism terminated by two six-sided Pyramids, Bipyramidal Hexagonal Prism, bounded by eighteen Planes (fig. 12, Plate VII.).

This is a *simple* form, being entirely composed of *biaxial* planes; some however are primary, some secondary, and hence it is termed a *mixed* form.

The six lateral planes of the Hexagonal Prism constitute one-half of the Primary Biaxial Form, whilst the remaining half is replaced by the double secondary planes belonging to the obtuse isosceles triangular dodecahedron last described.

This familiar form, so common in the oblique equiaxial genus, has already been sufficiently explained. Sulphuret of copper furnishes specimens of this form belonging to the regular system. The coincidence of the alternate terminal edges with the edges of the uniaxial form already explained, must be remembered as furnishing a very ready means of determining the primary form.

## Triaxial Forms.

*Primary Triaxial Form*

(X Y Z) or 1.1.1.

Synonyme: Octahedron, bounded by eight Triangular Planes (figs. 18, 22, 23, Plate X., figs. 1, 22, Plate XII.).

This form requires little additional explanation. Figs. 3 and 7, Plate VII. will illustrate its relationship to the primary uniaxial and biaxial forms. It will be observed that the edges of the octahedron bisect the biaxial planes, and that their directions coincide: this should be remembered in tracing the relationship of the imperfect and elongated triaxial forms more particularly illustrated in Plate XII.

The primary triaxial form is of great importance in ascertaining the position of the gubernatorial axes which are situated at the solid angles where four planes meet. The optic axes will be situated in some of the planes of the Octahedron, except in Genus 2, Class I.

### Imperfect Primary Triaxial Forms

$$(X \overset{\wedge}{Y} Z).$$

The unequal development of the planes of the primary triaxial form requires attentive consideration, inasmuch as an immense variety of crystals, more especially amongst the silicates, can only be understood by tracing the alterations thus introduced into the primary triaxial form.

By the increased development of *two* opposite planes the imperfect form, fig. 4, Plate XII., is produced. Many instances of this form occur in nature. Fig. 18, copied from Haüy, is the representation of a crystal of arseniate of copper, termed by that author "hexagonal lamelliforme." Fig. 21 represents a natural crystal of carbonate of lime, evidently derived from fig. 22, as shown by the dotted lines which have been added to the figure as copied from Bournon's work already quoted, and which also contains numerous other figures of imperfect primary triaxial forms occurring in carbonate of lime. This imperfect form distinguishes the crystals of what is termed Hexagonal mica, and occurs in oxide of copper and many other substances.

By the greater development of *four* planes the octahedron gradually approximates to the tetrahedron, fig. 10. Figs. 12 and 14 represent such imperfect forms as occurring in native copper; a group of such crystals is exhibited in fig. 16.

The extension of *six* planes converts the octahedron into forms approximating to the very acute rhombohedrons observed in carbonate of lime, termed by Haüy "contrastante" and "mixte," fig. 23, Plate XII.; and numerous examples of such imperfect forms might have been easily selected from Bournon's treatise had further illustration been considered requisite.

### Defective Primary Triaxial Forms.

#### *Hemihedral Primary Triaxial Form*

$$\frac{1}{2}(X\,Y\,Z).$$

Synonymes: Tetrahedron, Hemioctahedron, bounded by four Triangular Planes. Fig. 10, Plate XII.

The complete obliteration of four planes of any octahedron by the overwhelming development of the other four planes produces a tetrahedron or four-sided solid, as already described. The gubernatorial axes will be situated in the lines bisecting two opposite edges, as may be understood by referring to figs. 10, 12 and 14.

*Three-Quarter Primary Triaxial Form*

$$\frac{3}{4}(X\,Y\,Z).$$

Produced by the extension of six planes obliterating the remaining two planes of the octahedron, as before explained, the result being a parallelopiped remarkable for the acuteness of its configuration (fig. 23, Plate XII.).

## Elongated Primary Triaxial Forms.

*Biaxially Elongated Perfect Primary Triaxial Form*

$$(\overline{X}\,\overline{Y}\,Z).$$

Synonyme: Quadrangular Prism with dihedral summits, bounded by eight Planes. (Figs. 10 and 11, Plate VIII., figs. 24, 25, 26, Plate X., fig. 2, Plate XII.)

This form is of great importance, as prevailing most extensively in the salts crystallizing in the oblique rectangular system, such, for instance, as the sulphates of baryta and strontian. When this form is once made familiar to the eye, it will be observed as the foundation of numerous modifications, the figures of which, occurring in different works, will be easily recognised by reversing their position. To find the position of the gubernatorial axes, the octahedron must be reduced to its normal dimensions, as illustrated (figs. 24, 25, 26, 28, Plate X.).

A frequent modification of this form is the Triuniaxial form $\frac{1}{3}(\overline{X}\,\underline{Y}\,\underline{Z}) + (\overline{X}\,\overline{Y}\,Z)$, produced by the presence of two uniaxial planes generating a six-sided prism (figs. 27 and 28, Plate X., and fig. 3, Plate XII.). This might be confounded with the biaxial hexagonal prism, but can be known by its dihedral terminations, as also very frequently by the existence of cleavage parallel to the uniaxial planes.

*Biaxially Elongated Imperfect Primary Triaxial Forms*

$$(\overline{X}\,\overset{\wedge}{\overline{Y}}\,Z).$$

The elongation of imperfect primary triaxial forms produces a variety of crystals so unlike their original octahedron, that until the method of relationship is well understood, such forms are extremely difficult of recognition. It is for this reason that a variety of examples are delineated in Plate XII., which will, it is hoped, sufficiently elucidate these forms, which have never been hitherto properly explained.

Since, as before stated, each edge of the octahedron coincides with the biaxial direction, and since elongation of the primary triaxial form can take place in any biaxial direction, it is apparent that a variety of configurations may result, according to which edge of the imperfect form coincides with the axis of elongation. Thus, fig. 5 results from elongation along the vertically placed edges of fig. 4, fig. 8 from fig. 7, 15 from 14, 13 from 12, and 10 from 11. It must however be observed that figs. 7, 10, 12 and 14 do not possess a perfect zone of planes parallel to the axis of elongation, in consequence of the imperfect development of the triaxial form; according, therefore, to the law of elongation before laid down, such *simple* forms are incapable of elongation, and it is only when they are converted into composite forms (by the introduction of uniaxial planes to complete the zone) that such crystals can be properly elongated; all this will, it is hoped, be sufficiently explained by studying Plate XII. The introduction of two opposite uniaxial planes is extremely common in the elongated primary triaxial form, even in those cases where it is not absolutely requisite, for the reason referred to. It is thus that the triuniaxial tabular crystals, figs. 27 and 28, Plate X., so frequently observed in sulphate of baryta, are produced. Figs. 3, 6, 8, 9, 13 and 15, Plate XII. are elongated triuniaxial forms, frequent amongst the silicates when derived from an oblique rectangular disposition of the gubernatorial axes. The figures 1 to 20 in Plate XII. all belong to the rectangular equiaxial or regular system; and when it is observed how much the primary triaxial form is distorted and obscured even in the regular system, it is easy to understand the greater distortion which must necessarily result from an oblique disposition of one or more of the gubernatorial axes. Fig. 9 represents the manner in which the greater development of the uniaxial planes of fig. 8 tends to the production of the hexagonal prism with sloping terminal planes, observable in sulphate of copper and many other salts. Crystals similar to figs. 8 and 9 occur also in axinite. The peculiar flatness and greater development of one side of the crystal, so observable both in axinite and sulphate of copper, may be explained by figs. 11, 13 and 15. These two substances do not belong to a doubly oblique primary form, as commonly supposed, but, like the majority of the salts, to the Oblique Rectangular Class.

The first clue to the peculiarities of these elongated imperfect primary triaxial forms was derived by the author from observing the natural groups of crystals of native copper figured Plate XII. figs. 16 and 17, which last are evidently

nothing more than an elongation of the imperfect primary triaxial form represented, fig. 16.

The formula of fig. 3 is

$$(\overline{X}\,Y\,Z)+\frac{1}{3}(\overline{X}\,\underline{Y}\,\underline{Z});$$

and of figs. 6, 8, 13 and 15,

$$(\overline{X}\,\underset{\wedge}{\overline{Y}}\,Z)+\frac{1}{3}(\overline{X}\,\underline{Y}\,\underline{Z}).$$

Of fig. 9, the formula is

$$\frac{3}{4}(\overline{X}\,\underset{\wedge}{\overline{Y}}\,Z)+\frac{1}{3}(\overline{X}\,\underline{Y}\,\underline{Z}).$$

Fig. 12, Plate XI., representing the crystal of pyroxene, before referred to, is an elongated ternobiaxial form, also common amongst the silicates; its formula is

$$(\overline{X}\,\underset{\wedge}{\overline{Y}}\,Z)+\frac{1}{3}(X\,Y\,\underline{Z}).$$

Figs. 19 and 20, Plate XII., exhibit the manner in which a triuniaxial truncated double hexagonal pyramid may originate from the primary triaxial form.

## Secondary Triaxial Forms.

$$\begin{pmatrix} X & Y & Z \\ x & y & z \end{pmatrix}.$$

### *Trigonal Treble Triaxial Form*

$$3\begin{pmatrix} X & Y & Z \\ 1 & 1 & x \end{pmatrix}.$$

Synonymes: Octotriahedron, Pyramidal Octahedron, Triakisoctahedron, Pyramidal Octahedric Icositesserahedron, Octahedral Trigonal Icositetrahedron, Trigonal Trisoctahedron, bounded by twenty-four Triangular Planes. Ex., fig. 24, Plate VIII.

In this form each face of the primary octahedron may be supposed to be replaced by a three-sided pyramid, the planes of which cut two axes at their normal length and the third axis at a distance indicated in the following table of forms said to exist.

| | Distance at which planes cut axes. |
|---|---|
| 1st Form . . . | 1, 1, $1\frac{1}{3}$ |
| 2nd ... . . . | 1, 1, $1\frac{1}{2}$ |
| 3rd ... . . . | 1, 1, $1\frac{2}{3}$ |
| 4th ... . . . | 1, 1, 2 |
| 5th ... . . . | 1, 1, 3 |
| 6th ... . . . | 1, 1, 4 |

Fluor spar and galena may be quoted as occurring in this form. The author has observed an approximation to this form in carbonate of lime.

*Tetragonal Treble Triaxial Form*

$$3\begin{pmatrix} X\,Y\,Z \\ 1\,x\,x \end{pmatrix}.$$

Synonymes: Trapezohedron, Tetragonal Trisoctahedron, Icositetrahedron, Trapezoidal Icositetrahedron, Tetragonal Icositetrahedron, bounded by twenty-four Trapezoidal Planes. Ex., fig. 21, Plate X.; figs. 9, 10 and 11, Plate XI.

This form, as explained by figs. 19, 20 and 21, Plate X., consists in replacing the solid angles of the parallelopiped by three facets, which in the perfect form have a trapezoidal outline; hence each face of the primary octahedron is replaced by three such trapezoidal facets, whilst each face of the primary parallelopiped is replaced by *four* such faces, their central point of union corresponding to the gubernatorial axes. This form might also be considered as resulting from the replacement of each face of the primary dodecahedron by a four-sided pyramid.

This form differs from the preceding trigonal form in cutting only one axis at its normal length and the other two axes at a greater distance, as described in the subjoined table, based chiefly on the observations of other authors.

| | Distance at which planes cut axes. |
|---|---|
| 1st Form . . . . . | 1, $1\frac{1}{4}$, $1\frac{1}{4}$ |
| 2nd ... . . . . | 1, $1\frac{1}{2}$, $1\frac{1}{2}$ |
| 3rd ... (most common) . | 1, 2, 2 |
| 4th ... . . . . | 1, $2\frac{2}{3}$, $2\frac{2}{3}$ |
| 5th ... (common) . . . | 1, 3, 3 |
| 6th ... . . . . | 1, 4, 4 |
| 7th ... . . . . | 1, 6, 6 |
| 8th ... . . . . | 1, 12, 12 |

This form is of frequent occurrence. Garnet, analcime and carbonate of lime present examples thereof. The gubernatorial axes will be found at the points where four planes meet.

A great variety of imperfect crystals of this form occur in nature, especially in carbonate of lime, more particularly resulting from the greater development of the planes marked *a*, tending to the double pyramidal form. When these planes are developed so as to obliterate the remaining planes, the resulting defective form is in some degree dependent on the class to which the Trapezohedron belongs. Thus in the

Rectangular Class a double eight-sided pyramid, fig. 11, Plate XI., is the consequence, its formula being

$$\frac{2}{3}\left(3\begin{pmatrix}X\,Y\,Z\\1\,2\,2\end{pmatrix}\right).$$

In the Oblique Class, fig. 10, Plate XI., the triangular dodecahedron already alluded to is produced. Fig. 13, Plate VII. exhibits such form enclosed in a skeleton of the biaxial dodecahedron. Its formula is

$$\frac{1}{2}\left(3\begin{pmatrix}X\,Y\,Z\\1\,x\,y\end{pmatrix}\right).$$

*Sextuple Triaxial Form*

$$6\begin{pmatrix}X\,Y\,Z\\1\,x\,y\end{pmatrix}.$$

Synonymes: Hexoctahedron, Octohexahedron, Hexakisoctahedron, Tetracontaoctahedron, bounded by forty-eight Triangular Planes. Ex., fig. 21, Plate VIII.

This form originates in six secondary triaxial planes placed on the solid angles of the parallelopiped, as shown in figs. 20 and 21, Plate VIII.; the result is, that each plane of the primary parallelopiped is replaced by a pyramid of eight sides, whilst the faces of the primary octahedron are surmounted by a pyramid of six sides. The planes of the primary dodecahedron are replaced by a pyramid of four planes, and the exterior edges of these four planes, constituting the base of the pyramid, correspond to the edges of the primary Biaxial planes, thus marking out, as it were, the primary dodecahedron.

In this form one axis is cut at its normal length, the other two axes each differently but at a prolonged distance. There seems some little difficulty in presenting an accurate table of the forms which have been actually observed, owing to the discrepancy existing in the observations recorded. The following however are said to occur:—

| | Distance at which planes cut axes. |
|---|---|
| 1st Form . . . . | 1, $1\frac{1}{2}$, 3 |
| 2nd ... . . . . | 1, $1\frac{1}{3}$, 4 |
| 3rd ... . . . . | 1, 2, 4 |
| 4th ... . . . . | 1, 2, 6 |
| 5th ... . . . . | 1, $2\frac{1}{3}$, 7 |

Garnet and fluor spar furnish examples of this form; but

the author has not hitherto observed any instance of its occurrence in the oblique system.

The gubernatorial axes are situated at the points where eight planes meet.

## General Observations.

The foregoing synopsis contains an account of predominant forms sufficiently extensive to illustrate the general relationship of all crystals, and any crystal naturally occurring may be referred to one or other of the forms therein described as a basis, and thence the position of the gubernatorial axes and the primary form may be determined. The minor modifications are of little importance, and if not conducive to a knowledge of the real position of the gubernatorial axes, may be safely neglected. It is to be regretted that so much time and attention has been devoted to the measurement of the inclination of facets of no importance, whilst the plane angles have been altogether neglected.

It is surprising how few are the forms from which the numerous modifications occurring in nature really derive their parentage. To have followed such forms through all their gradations of unequal development would have required many hundred figures; and although the author possesses abundant materials for such purpose, it would be obviously inconsistent with the immediate purpose of the present paper still further to extend its illustrations.

The manner in which the author has arrived at the conclusions herein contained, has been,—first, by observing the various gradations through which the forms may be traced in natural crystals, and next by examining their optic axes as the only means whereby the true position of the gubernatorial axes can be positively deduced. If the principle be admitted that the optic axes do lie in the resulting diagonal of the parallelogram of forces, and if again the gubernatorial axes be identified with the lines of aggregating force, it is obvious that the examination of the position of the optic axes furnishes a means whereby to test the correctness of any deductions as to the relationship of a given form to the gubernatorial axes.

The author cannot conclude this portion of the subject without inviting the attention of chemists to the method now developed, as furnishing the only certain basis on which the doctrines of isomorphism, &c. can rest, and the true connexion of chemical constitution with crystalline form be established. Apologising to the members of the Society for the very long

delay occurring in the printing of this paper, he trusts that his anxious desire to render it sufficiently complete to answer the purpose of practical application will atone for any inconvenience which may have resulted therefrom.

*Description of a Double Refracting Goniometer.*

The goniometer invented by the author, with a view to remove many of the difficulties incident to the instruments heretofore in use, is represented in Plate XIII. Amongst the peculiar advantages of this instrument may be enumerated its capability of measuring opake and imperfect crystals, also microscopic crystals, and crystals in the interior of transparent media. It is equally applicable to the largest crystals, and will measure angles without removing the crystal from a specimen, provided only the whole is placed on a suitable adjusting stage*. The instrument depends on the application of a doubly refracting prism, either of Iceland spar or of quartz, of such a thickness as will only partially separate the two images of the angle which it is proposed to measure.

Premising that the goniometer may be either mounted as a separate instrument or attached to a microscope, it is proposed to describe it as when fitted to a body of the improved compound microscopes in common use. The same letters will be used for the corresponding parts in figs. 1 to 6, Plate XIII., which represents the various parts of the goniometer fitted up as the eye-piece of a microscope, together with those of the adjusting stage to support the crystal which is intended to fix upon the traversing stage of the microscope.

Fig. 1 is a perspective view of the goniometer, and fig. 2 is a section of the same. At (*a*) is an achromatic prism of double refracting Iceland spar—a Rochon's prism of quartz may be substituted; (*b*) is a brass tube containing the prism, with a round aperture forming the cap of the eye-piece, and sliding stiffly on the tube (*c*) attached to the arm (*d*) carrying the vernier of the graduated circle (*h*). At (*f*) is an achromatic eye-piece, either Huygenian or positive, sliding stiffly or screwing into the tube (*g*) which fits into the tubular body of the microscope. If the crystal is large and no magnifying power required, this eye-piece may be dispensed with; a single lens of long focus may occasionally be substituted with advantage. The vernier has a clamping screw at (*i*) and an adjusting screw at (*k*). A reading microscope, placed at (*e*),

* This goniometer may be also employed to measure distant angles, such, for instance, as the inclination of strata, or the lines required in a perspective drawing, and only requires to be attached to a telescope, or mounted on a suitable stand.

is attached to the vernier. Fig. 3 is the adjusting stage to support the crystal whose angles are to be measured, and fig. 4 is a section of the same. The crystal may either be attached by Canada balsam or wax to a glass, or blackened ivory plate (*l*) dropping into the ring (*m*), which again fits into the ring (*n*), or the crystal may be conveniently held by the clamping arms in fig. 6, attached to a ring, also fitting into the plate (*n*). Two of these arms have very small cups at their extremity fitted with a piece of India rubber or cork, by means of which they can be pressed against a crystal without bruising it. The third arm has a small fork at its extremity, which turns round on the end of the arm at (*x*) in any direction to suit the crystal. The arrangement of screws and guides shown in the drawing is for the purpose of sliding the arms to and from the centre where the crystal is to be fixed. Fig. 5 is another ring fitting into (*n*) with two light springs to hold a slip of glass on which to fix a crystal when desired, or to carry one of the ordinarily mounted microscopic specimens.

(*p*), figs. 3 and 4, is a semicircle attached to the ring (*n*), which is centred on two screws at *t*, *t'*, passing through two uprights, so that it may be inclined at any angle and fixed by the clamping screw (*r*). This semicircle may be graduated, in which case it can also be employed for determining the inclination of the optic axes by polarized light. Not only can the plate (*m*) be revolved in any direction within the ring (*n*), and set to any inclination by the semicircle (*p*), but the whole ring (*o*) carrying the upright supports may also be revolved around the short tube shown in the section at (*u*) upon the plate (*s*) which fits upon the traversing stage of the microscope. The ring (*o*) may also be graduated, if thought useful, and thus rendered convenient for investigations by means of polarized light.

When a crystal, or any angle thereof, is viewed through the prism attached to the goniometer, two images thereof are produced by revolving the prism, which, with respect to each other, may be made to occupy various relative positions, as shown, for example, in figs. 7, 8, 9. Let *a b c*, fig. 7, be the angle to be measured, the crystal being adjusted properly, as hereinafter explained. Place the vernier at zero, and there clamp it fast; then revolve the tube (*b*) containing the prism until the lines forming one side of the angle to be measured coincide in both images, as for instance the lines *a b*, *a' b'*, fig. 8; then release the vernier and revolve it on the graduated circle until the two lines forming the other side of the angle *b c*, *b' c'* also coincide, fig. 9. The amount of rotation

thus obtained is the measure of the angle, or its complement according to the direction in which the vernier is moved. Instead of starting from zero, it is of course sufficient to take the difference of the readings in the two positions.

There are two descriptions of angles, the one sort being the plane angles produced by the lines forming the edges of the planes, the other sort being the angles representing the inclination of the planes themselves to each other.

When a plane angle is to be measured, it is necessary that the two lines or edges forming it should be both situated in a plane perfectly horizontal, that is perpendicular to the axis of vision. The stage, fig. 3, furnishes every facility for this adjustment, which may be known to be perfect by using a suitable object-glass and observing that every portion of both lines remains exactly in focus on traversing the stage.

When the inclination of two planes is to be measured, they must be so adjusted that their line of junction is parallel to the axis of vision, or, to use a familiar expression, they must be taken out of winding, as it is termed. A very little practice will satisfy the observer that these adjustments may be readily accomplished by the stage in question.

Similar adjustments may be effected, although somewhat more difficult, by using the forceps commonly sold with the compound microscopes, more especially the three-pronged forceps made by Smith.

The author cannot too strongly insist on the importance of the microscope in examining the surface of the planes of crystals subjected to measurement, convinced as he is that obliquity in many cases arises not only from conchoidal fractures, but also from imperfect laminæ elevating one portion of a plane, and yet allowing a very tolerable reflection when measured by the reflective goniometer. Another source of error sometimes arises from not observing that the planes measured are those of macled or aggregated crystals, and thus furnish angles which would not exist in a distinct crystal.

### *Calculation of Angles.*

The inclination of the gubernatorial axes (the grand object of crystallographic research) may be frequently deduced from calculations founded on the known relationship of various forms, employing as data the angles obtained by admeasurement in particular crystals.

The application of the principles of trigonometrical calculation to the investigation of crystalline forms has already been ably treated of by other authors; and a mere repetition of problems, the solution of which may be elsewhere found,

would probably be deemed superfluous. As some however may be interested in the subject who are not very conversant with such investigations; and as there are certain problems more immediately connected with the views developed in the present paper; the author hopes, that a few observations, together with some examples of the use of formulæ, derived from Spherical Trigonometry, will not be considered inappropriate.

By reference to what has already been stated, respecting the uniaxial form, and by examining the figures thereof contained in the various Plates, it will be apparent, that since each of its six planes cuts one axis and is parallel to the other two, the *edges* of the planes themselves *coincide in dimension and direction with the axes.* Hence if any three adjacent edges of a simple uniaxial form be chosen, such three edges will represent the lengths and inclinations of its three gubernatorial axes.

The inclination of any two edges or lines bounding a plane constitutes (as before explained) what is termed a *plane angle.* Thus C O B, C O A, A O B represent three adjacent plane angles of the supposed uniaxial parallelopiped, fig. 1, Plate VI., and therefore represent also the inclination of the gubernatorial axes. A *plane angle,* that is, the inclination of two lines bounding a plane, must not be confounded with the angle expressing the *inclination of the planes themselves.* That is, returning to fig 1, Plate VI., the plane angle C O A representing the inclination of the edge C O with O A must not be confounded with the angle B, representing the inclination of the plane P upon the plane P″.

Plane angles cannot be measured by reflecting goniometers. Hence the observations usually recorded give the inclinations of the planes themselves, from which however the plane angles may be calculated by the aid of Spherical Trigonometry and Logarithmic Tables.

The Crystallonome already described will greatly aid the student in rightly conceiving the questions to be solved by the aid of Spherical Trigonometry; and in fact by using the compass-points and a circular protractor, or line of chords, many of the problems hereafter propounded may be solved by the instrument itself, which will at all times afford a convenient check upon the calculations.

As carbonate of lime is a substance whose crystalline characters have been most largely treated of, and as it occurs in an immense variety of form, and affords abundant material for illustrating the principles contained in the foregoing paper, it will be selected as the medium of illustration.

*The inclination of the gubernatorial axes being given, to calculate the inclination of the planes of the uniaxial form.*

Since, as already explained, the inclinations of the three gubernatorial axes correspond to the three adjacent plane angles of the uniaxial form, the question resolves itself into the determination of the inclination of the planes of a parallelopiped, of which the plane angles are given.

Let fig. 1, Plate VI., represent such a parallelopiped, of which the plane angles C O A, C O B, A O B (corresponding to the inclinations of the gubernatorial axes) are determined. From the centre O, where the three angles meet, describe the spherical triangle C A B; then, adopting the usual notation,

the side $a$ will be $= \angle$ C O B.
... $b$ ... $= \angle$ C O A.
... $c$ ... $= \angle$ A O B.

The angle A will be = inclination of plane P′ upon plane P″.
... B ... ... P ... P″.
... C ... ... P ... P′.

Supposing, for example, fig. 1 represents the Ordinary Obtuse Bisecting Rhombohedron of carbonate of lime, the three plane angles of which, when measured by a goniometer, are found to be all equal, viz. 102°.

As, in consequence of the equal inclination of the axes, the planes will be all equally inclined on each other, it is sufficient to determine any one of them, as, for instance, the inclination of P′ on P″ = angle A.

Then by the well-known formula

$$\sin \tfrac{1}{2} A = R \sqrt{\frac{\sin \tfrac{1}{2}(a+b-c) \sin \tfrac{1}{2}(a+c-b)}{\sin b \times \sin c}}$$

$a$ = inclination of edges C O and O B.
= inclination of equatorial axes.
= 102°.
$b$ = inclination of edges C O and O A.
= inclination of an equatorial and vertical axis.
= 102°.
$c$ = inclination of edges A O and O B.
= inclination of vertical axis with the other equatorial axis.
= 102°.

Therefore

$$\sin \tfrac{1}{2}(a+b-c) = \frac{102+102-102}{2} = 51° ;$$

similarly, $\sin \frac{1}{2}(a+c-b)=51°$;

but $\sin 51° \times \sin 51° = \log \sin 51° + \log \sin 51°$

$$\begin{array}{r} 9{\cdot}8905026 \log \sin 51° \\ 9{\cdot}8905026 \log \sin 51° \\ \hline = 19{\cdot}7810052 \end{array}$$

$\sin b \times \sin c = \sin 102° \times \sin 102° = \log \sin 102° + \log \sin 102°$

$$\begin{array}{r} 9{\cdot}9904044 \log \sin 102° \\ 9{\cdot}9904044 \log \sin 102° \\ \hline = 19{\cdot}9808088 \end{array}$$

$$\begin{array}{rr} & 19{\cdot}7810052 \\ \log \text{Rad.}^2 = & 20{\cdot} \\ \hline & 39{\cdot}7810052 \\ & 19{\cdot}9808088 \\ \hline \text{Extracting the square root } 2) & 19{\cdot}8001964 \\ \hline \sin \frac{1}{2}\text{A} = & 9{\cdot}9000982 = \log \sin 52° 36' 32'' \end{array}$$

therefore $\frac{1}{2}\text{A} = 52° 36' 32''$,

and $\text{A} = 105° 13' 4''$.

The rhombohedron being of the bisecting species, the inclination of its planes may also be determined as follows: Bisect the rhomb by a plane perpendicular to P, as in fig. 2, Plate VI., and construct the right-angled spherical triangle C A B. Then

$$a = \frac{102}{2} = 51$$

$$c = 102°.$$

Next ascertain the inclination of the vertical axis upon the equatorial plane (or, which is in fact the same thing, the inclination of the edge A upon the plane P, that is, of the plane angle formed by the lines A and C, being what the Comte de Bournon terms the salient angle), that is, the side $b$ of the spherical triangle C A B.

Thus,
$$\cos b = \frac{\text{R.} \times \cos c}{\cos a}$$

$$= \frac{\text{R.} \times \cos 102°}{\cos 51°}$$

$$\begin{array}{rl} 19{\cdot}3178789 & \log \text{R.} \times \log \cos 102° \\ 9{\cdot}7988718 & \log \cos 51° \\ \hline = 9{\cdot}5190071 & = \log \cos 70° 42' 30'', \end{array}$$

whence $b = 70° 42' 30''$.

Lastly, $$\sin B = \frac{R. \times \sin b}{\sin c}$$

$$= \frac{R. \times \sin 70^\circ\ 42'\ 30''}{\sin 102^\circ}$$

$$\begin{array}{ll} 19{\cdot}9749025 & \log \text{Rad.} \times \sin 70^\circ\ 42'\ 30'' \\ 9{\cdot}9904044 & \log \sin 102^\circ \\ = \overline{9{\cdot}9844981} & = \log \sin 105^\circ\ 13'\ 4'', \end{array}$$

whence $B = 105^\circ\ 13'\ 4''$.

*The inclination of the planes of a primary uniaxial parallelopiped being given to determine the inclination of the gubernatorial axes.*

Construct the spherical triangle C A B, fig. 1, Plate VI., as before, then employing the same notation, the inclination of the gubernatorial axes will be represented by the sides $a$, $b$, $c$, as before explained, which may be calculated by the following formulæ:—

$$\sin \tfrac{1}{2} a = R.\sqrt{-\frac{\cos \frac{1}{2}(A+B+C) \times \cos \frac{1}{2}(B+C-A)}{\sin B \times \sin C}}$$

$$\sin \tfrac{1}{2} b = R.\sqrt{-\frac{\cos \frac{1}{2}(A+B+C) \times \cos \frac{1}{2}(A+C-B)}{\sin A \times \sin C}}$$

$$\sin \tfrac{1}{2} c = R.\sqrt{-\frac{\cos \frac{1}{2}(A+B+C) \times \cos \frac{1}{2}(A+B-C)}{\sin A \times \sin B}}$$

The inclination of the planes of a fragment of Iceland spar having been determined by the goniometer to be $105^\circ\ 3'\ 59''$ at $50^\circ$ temperature Fahr., according to the observations of Mitscherlich, it is proposed to determine the inclination of the axes.

The inclination of the planes being all equal, the sides $a$, $b$, $c$ will be evidently equal, as before, it is therefore sufficient to determine any one of them.

By the formula

$$\sin \tfrac{1}{2} a = R.\sqrt{-\frac{\cos \frac{1}{2}(A+B+C) \times \cos \frac{1}{2}(B+C-A)}{\sin B \times \sin C}}$$

$$\tfrac{1}{2}(A+B+C) = \frac{105^\circ\ 3'\ 59'' + 105^\circ\ 3'\ 59'' + 105^\circ\ 3'\ 59''}{2}$$

$$= 157^\circ\ 35'\ 58''$$

$$\tfrac{1}{2}(B+C-A) = \frac{105^\circ\ 3'\ 59'' + 105^\circ\ 3'\ 59'' - 105^\circ\ 3'\ 59''}{2}$$

$$= 52^\circ\ 31'\ 59''$$

$\cos\frac{1}{2}(A+B+C)=\cos 157^\circ\ 35'\ 58''$ log= 9·9659268
$\cos\frac{1}{2}(B+C-A)=\cos\ 52^\circ\ 31'\ 59''$ log= 9·7841204
19·7500472

$\sin B=\sin 105^\circ\ 3'\ 59''$ log= 9·9848086
$\sin C=\sin 105^\circ\ 3'\ 59''$ log= 9·9848086
19·9696172

$\therefore \cos\frac{1}{2}(A+B+C)\times\cos\frac{1}{2}(B+C-A)=19·7500472$
log Rad.$^2$=20·
39·7500472
$\sin B\times\sin C=19·9696172$
2)19·7804300

Hence $\sin\frac{1}{2}a=$ 9·8902150 = log sin 50° 57′ 11″
$\frac{1}{2}a=\ 50^\circ\ 57'\ 11''$
and $a=101^\circ\ 54'\ 22''$.

According to Bournon and Haüy's measurements,
$A=104^\circ\ 28'\ 40''$ $\quad a=101^\circ\ 32'\ 13''$;
and the inclination of the vertical axis is $71^\circ\ 33'\ 54''$.

According to Wollaston's measurement,
$A=105^\circ\ 5'\ 0''$ $\quad a=101^\circ\ 55'\ 0''$;
and the inclination of the vertical axis is $70^\circ\ 51'\ 48''$.

Assuming that in the primitive uniaxial obtuse bisecting species of carbonate of lime the inclination of the axes, that is the plane angles,

$a$, $b$, $c$ } are each equal to 102°,

and that the inclination of the planes themselves, that is the angles,

A, B, C } are each equal to 105° 13′ 4″,

and that the inclination of the vertical axis upon the plane of the equatorial axes, or what Bournon terms the salient angle, is equal to 70° 42′ 30″, the remaining species may be calculated.

*Vertical Species.*

Fig. 5, Plate III. and fig. 4, Plate VI.

In this species the inclination of the plane P upon P′ becomes a right angle. Hence CAB is a right-angled spherical triangle, of which are known

$$\angle c = 90^\circ$$
$$\angle a = 102^\circ$$
$$\angle b = 70^\circ\ 42'\ 30''\text{;}$$

and the remaining plane angle $c$ may be determined from the formula

$$\cos c = \frac{\cos a \times \cos b}{R}$$
$$= \frac{\cos 102^\circ \times \cos 70^\circ\ 42'\ 30''}{10}$$
$$\begin{array}{r} 9{\cdot}3178789 \\ 9{\cdot}5190071 \\ \hline 18{\cdot}8368860 \\ 10{\cdot} \\ \hline 8{\cdot}8368860 \end{array} = \cos 86^\circ\ 3'\ 40''$$
$$c = 86^\circ\ 3'\ 40''.$$

*Intersecting Obtuse Species.*

Fig. 2, Plate III. and fig. 3, Plate VI.

Supposing the plane angle $c$ of the plane P″ to be 95° 28′, as in the 9th modification of M. Comte de Bournon, it is proposed to ascertain the plane angles of the remaining side P′, as also the angle of intersection.

Let the perpendicular plane coinciding with the vertical axis intersect the side $a'\,a$ at C, then describe the two right-angled spherical triangles, B′ A C, C A B.

Then $a' + a = 102^\circ$

$$\cos a = \frac{R \times \cos c}{\cos b}$$
$$= \frac{10 \times \cos 95^\circ\ 28'}{\cos 70^\circ\ 42'\ 30''}$$
$$\begin{array}{r} 18{\cdot}9789408 \\ 9{\cdot}5190071 \\ \hline 9{\cdot}4599337 \end{array} = \cos 73^\circ\ 14'\ 24''.$$

Therefore $a = 73^\circ\ 14'\ 24''$
and $a' = 28^\circ\ 45'\ 36''$
$a + a' = 102^\circ\ \ 0\ \ 0$

Next
$$\cos c' = \frac{\cos a' \times \cos b}{R}$$
$$= \frac{\cos 28^\circ\ 45'\ 36'' \times \cos 70^\circ\ 42'\ 30''}{10}$$

$$\begin{array}{r} 9{\cdot}9428228 \\ 9{\cdot}5190071 \\ \hline 19{\cdot}4618299 \\ 10 \\ \hline = 9{\cdot}4618299 = \log \cos 106^\circ\ 50'\ 7''. \end{array}$$

Therefore $c' = 106^\circ\ 50'\ 7''$

Supt. $= 73^\circ\ 9'\ 53''$.

*Intersecting Acute Species.*

Fig. 7, Plate III. and fig. 5, Plate VI.

Taking the Comte de Bournon's 16th modification, $c' = 98^\circ\ 41'$, and proceeding similarly,

here $a' + a = 78^\circ$

$$\cos a' = \frac{R \times \cos c'}{\cos b}$$

$$= \frac{10 \times \cos 98^\circ\ 41'}{\cos 70^\circ\ 42'\ 30''}$$

$$\begin{array}{r} 19{\cdot}1789001 \\ 9{\cdot}5190071 \\ \hline = 9{\cdot}6598930 = \log 62^\circ\ 48'\ 28'' \end{array}$$

whence $a' = 62^\circ\ 48'\ 28''$

$a = 15^\circ\ 11'\ 32''$

$a' + a = 78^\circ\ 0'\ 0''$

next $\cos c = \dfrac{\cos a \times \cos b}{R}$

$$= \frac{\cos 15^\circ\ 11'\ 32'' \times \cos 70^\circ\ 42'\ 30''}{10}$$

$$\begin{array}{r} 9{\cdot}9845508 \\ 9{\cdot}5190071 \\ \hline 19{\cdot}5035579 \\ 10 \\ \hline = 9{\cdot}5035579 = \log 108^\circ\ 35'\ 32'' \end{array}$$

Hence $c = 108^\circ\ 35'\ 32''$

Supt. $= 71^\circ\ 24'\ 28''$.

*Bisecting Acute Species.*

Fig. 8, Plate III. and fig. 6, Plate VI.

Here $a + a' = 78$

$$a = \frac{78}{2} = 39$$

$$\cos c = \frac{\cos a \times \cos b}{R}$$

$$= \frac{\cos 39^\circ \times \cos 70^\circ\ 42'\ 30''}{10}$$

$$\begin{array}{r} 9{\cdot}8905026 \\ 9{\cdot}5190071 \\ \hline 19{\cdot}4095097 \end{array}$$

$$= \frac{10}{9{\cdot}4095097} = \cos 75^\circ\ 7'\ 21''$$

$$c = 75^\circ\ 7'\ 21''.$$

*To ascertain the inclination of the vertical axis,* that is the angle which the vertical axis makes with the equatorial plane, or, as previously explained, the inclination of the edge A upon the plane P, being one of what Bournon terms "the principal salient angles," and Haüy "the angles of the principal section."

The manner in which this angle may be calculated in the obtuse bisecting species has already been illustrated. In an intersecting species, such as fig. 3, Plate VI., the inclination of the vertical axis, that is of the plane angle measured by the side *b* of the right-angled spherical triangle, CAB may be calculated from the formula

$$\sin b = \frac{\sin c \times \sin B}{R}.$$

The angle of intersection may be obtained from the formula

$$\tan a = \frac{\tan c \times \cos B}{R}.$$

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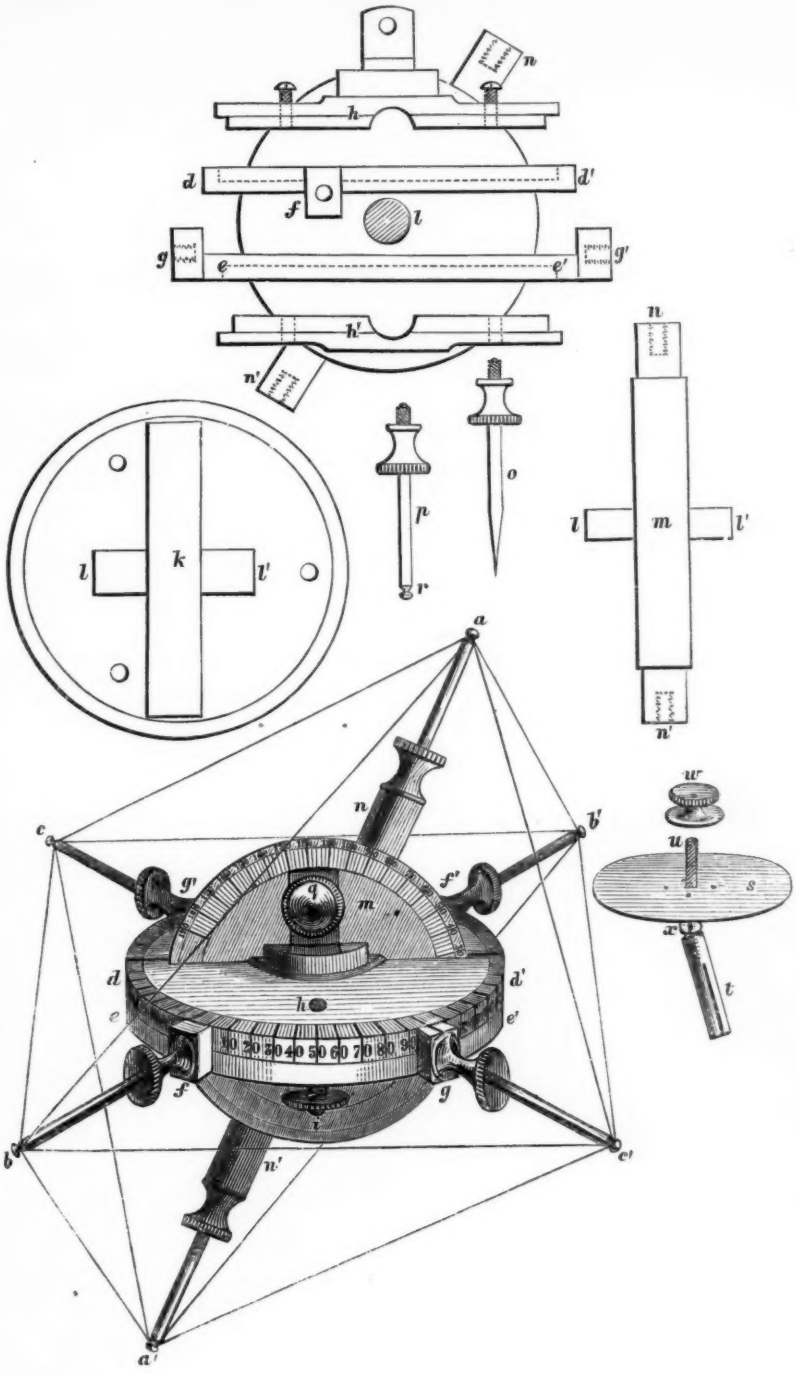
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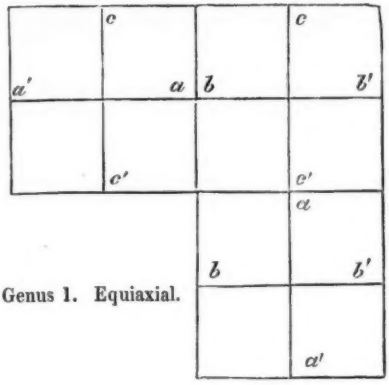
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# PLATE I.

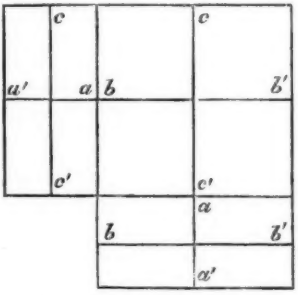


# PLATE II.

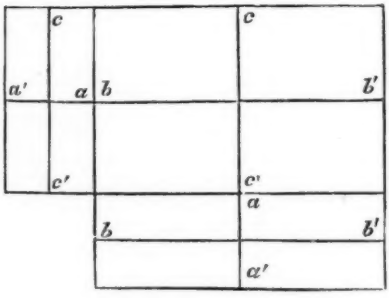
## Class 1. Rectangular.




Genus 1. Equiaxial.




Genus 2. Binequiaxial.




Genus 3. Inequaxial.

## Class 2. Oblique Rectangular.

Genus 1. Equiaxial.

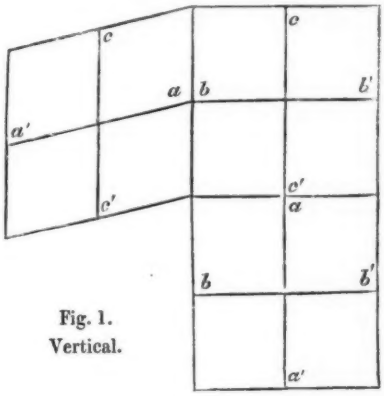



Fig. 1.
Vertical.

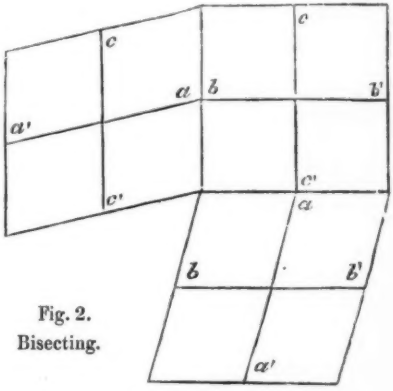



Fig. 2.
Bisecting.

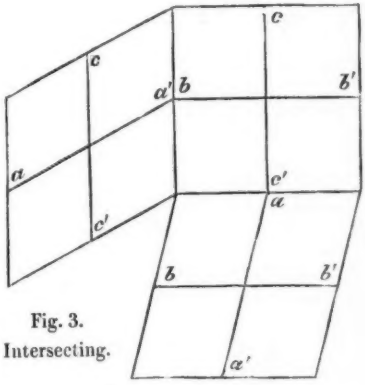



Fig. 3.
Intersecting.

# PLATE III.

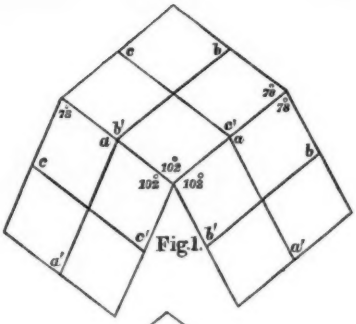


Fig.1.

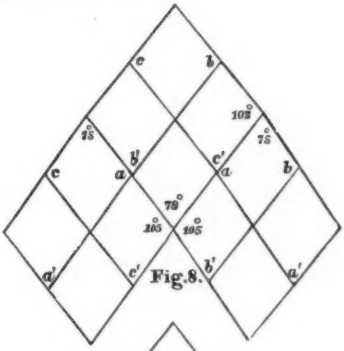


Fig.8.

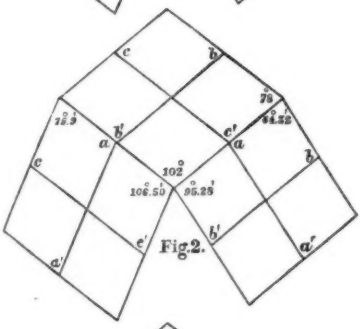


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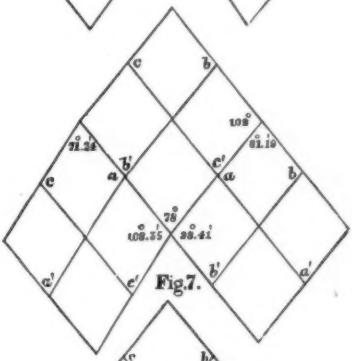


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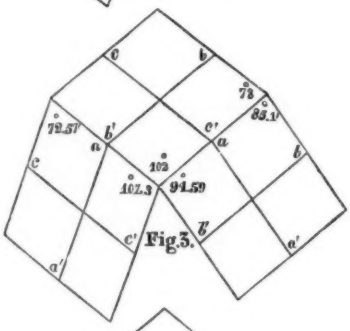


Fig.3.

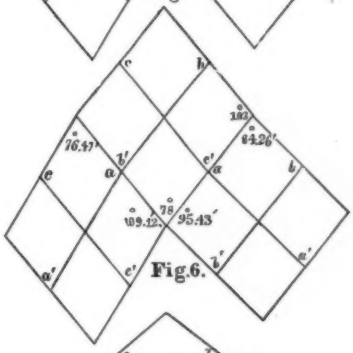


Fig.6.

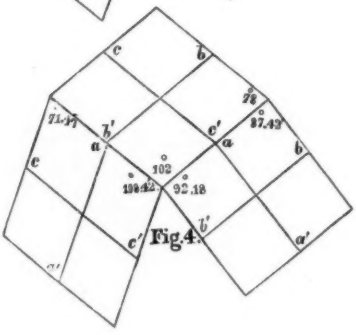


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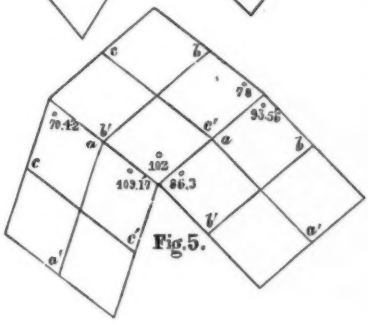


Fig.5.

# PLATE IV.

Fig. 9.

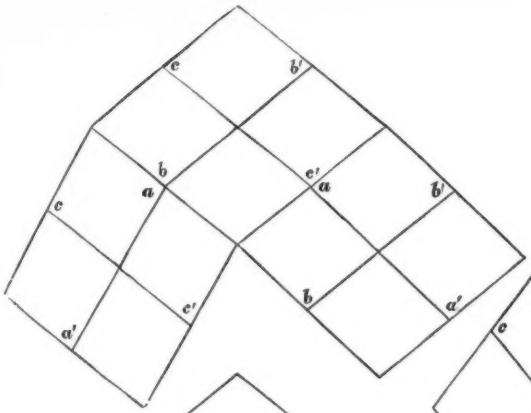
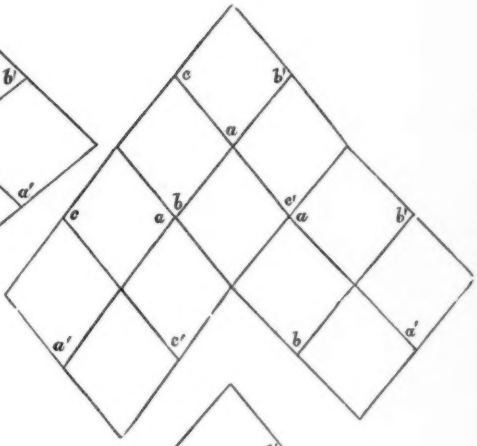



Fig. 10.



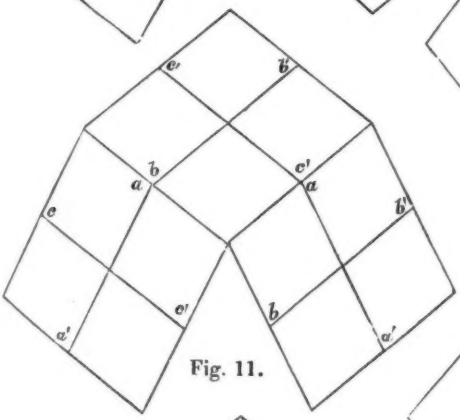




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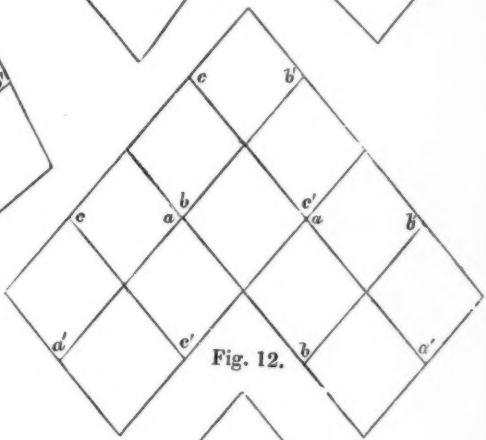



Fig. 12.

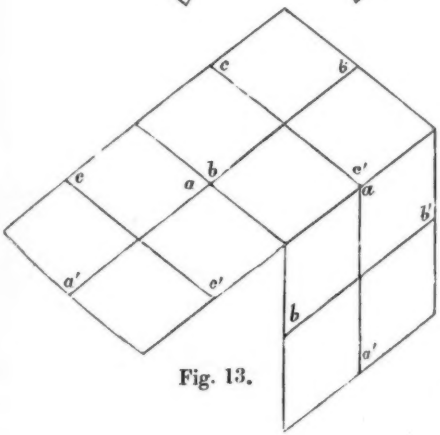



Fig. 13.

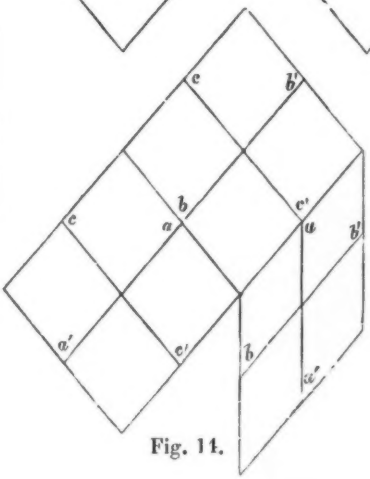
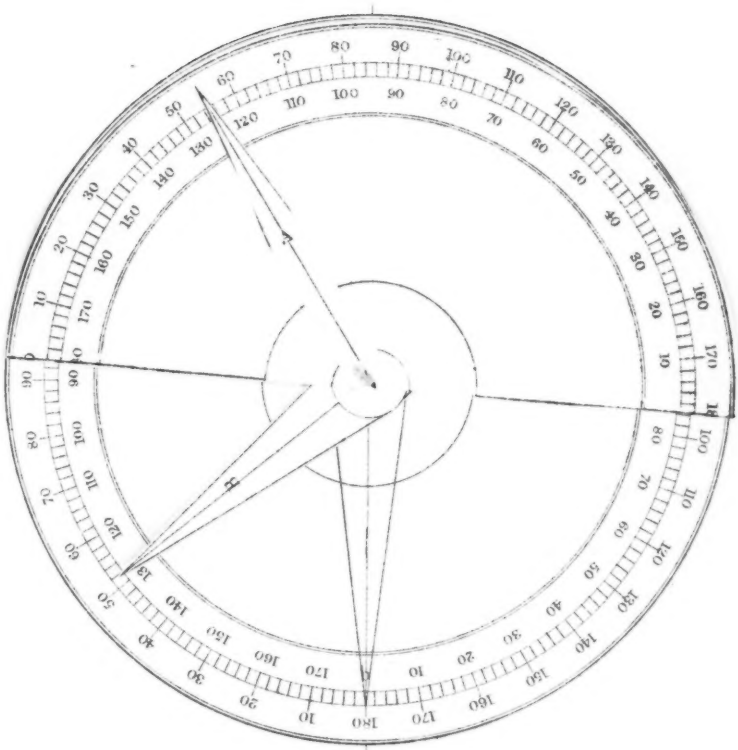



Fig. 14.



J. Basire sc.

# PLATE VI.

Fig. 1.

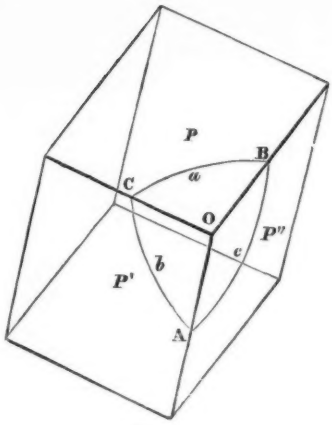



Fig. 2.

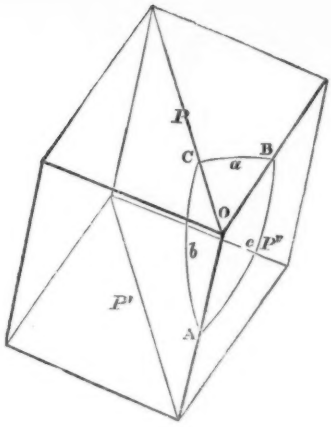



Fig. 3.

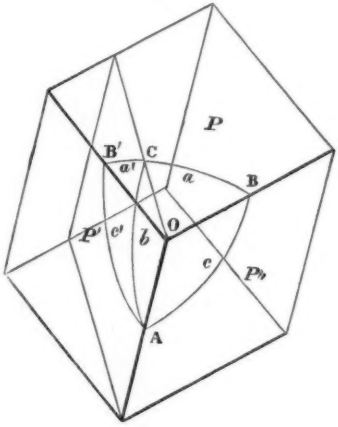



Fig. 4.

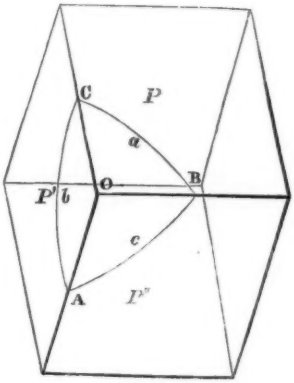



Fig. 5.

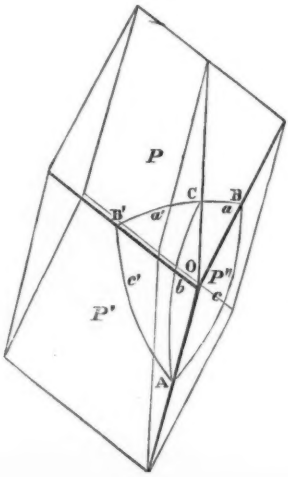
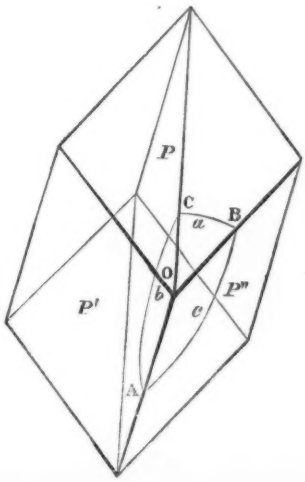
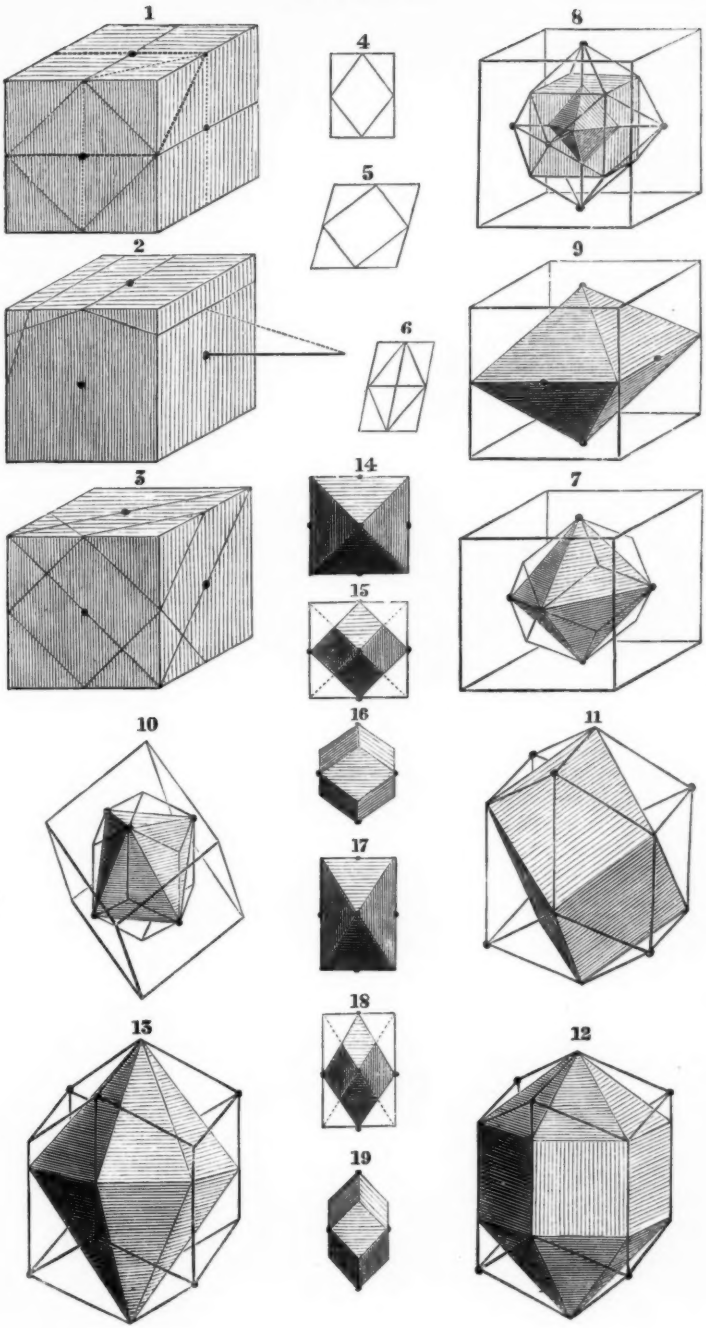


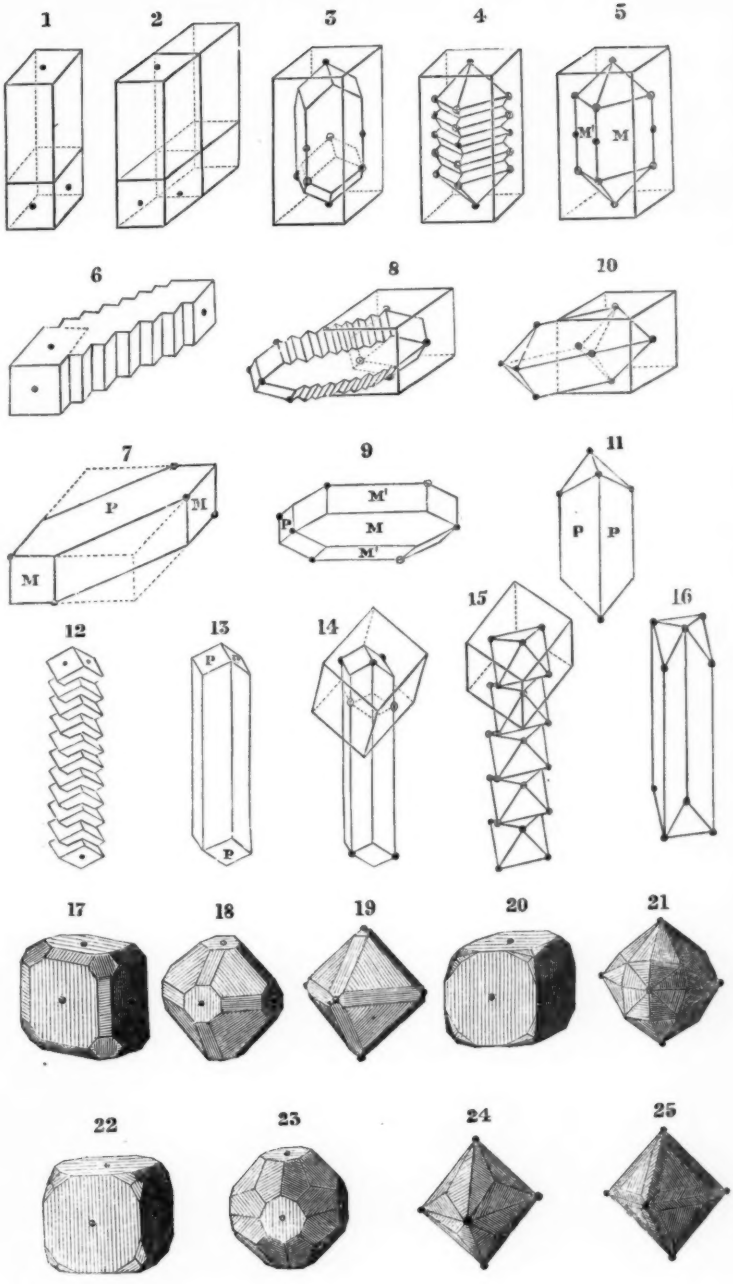

Fig. 6.



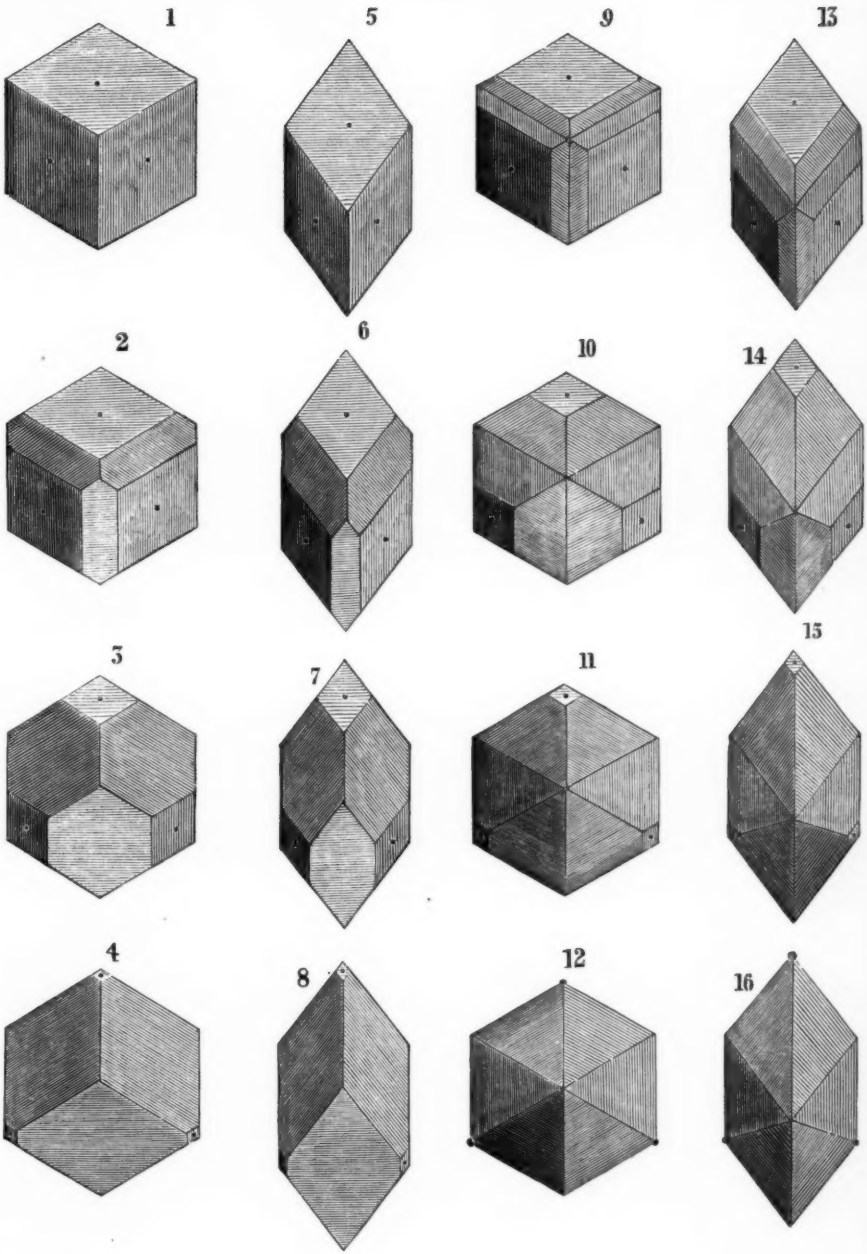
# PLATE VII.



# PLATE VIII.


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# PLATE IX.



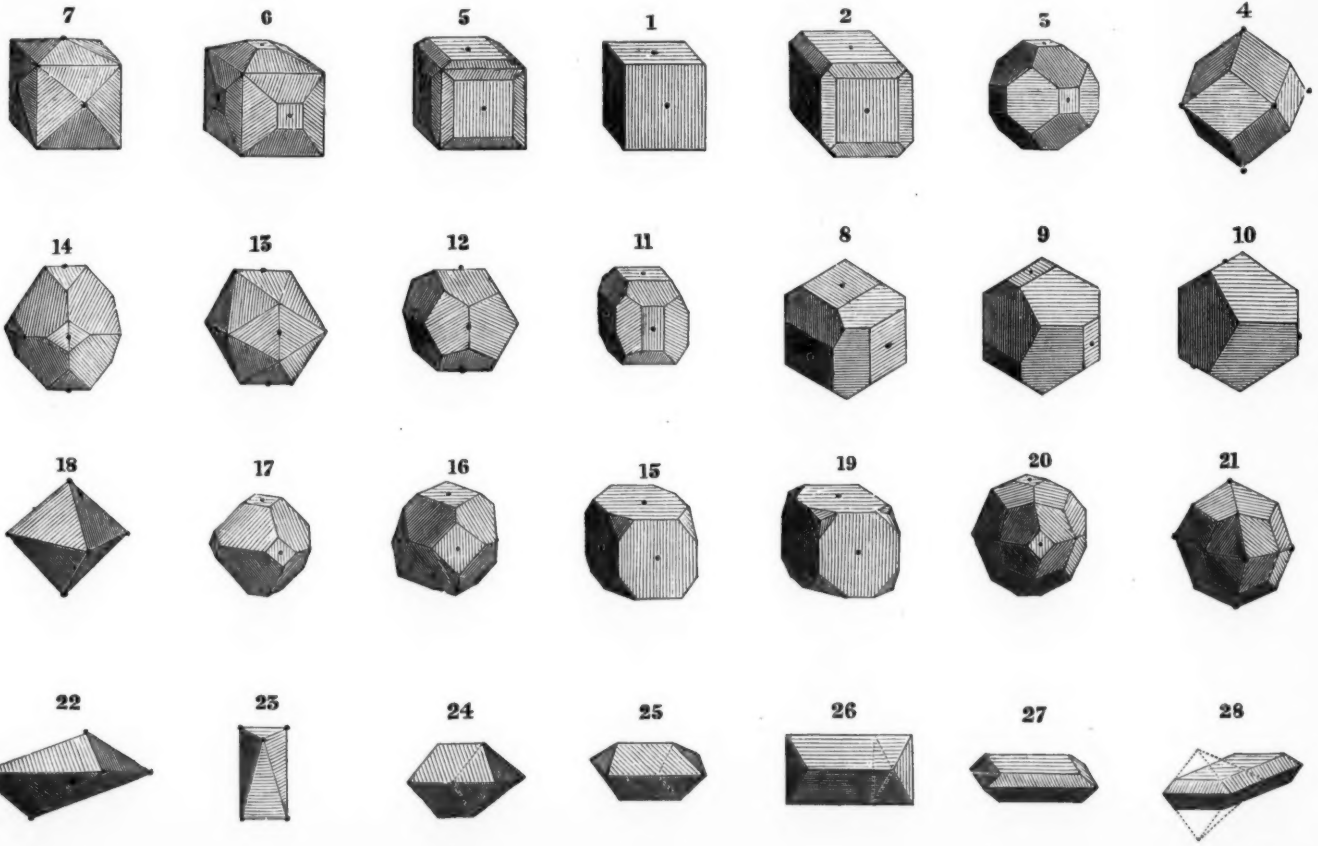
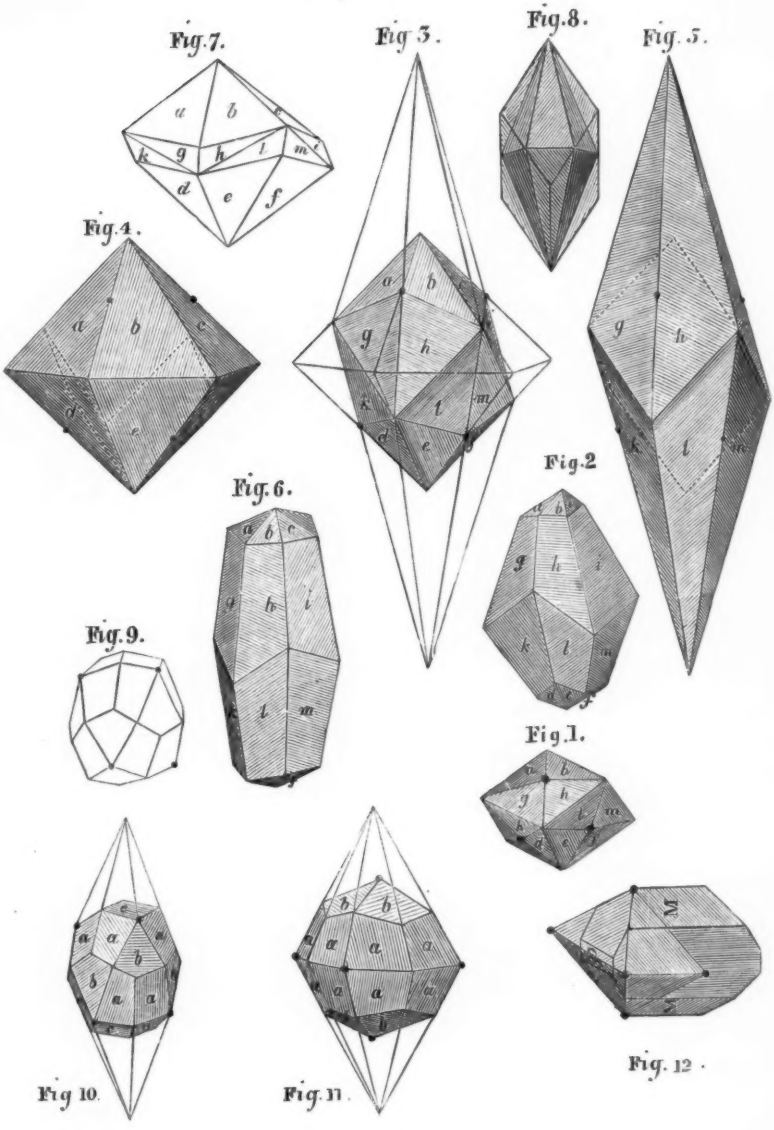
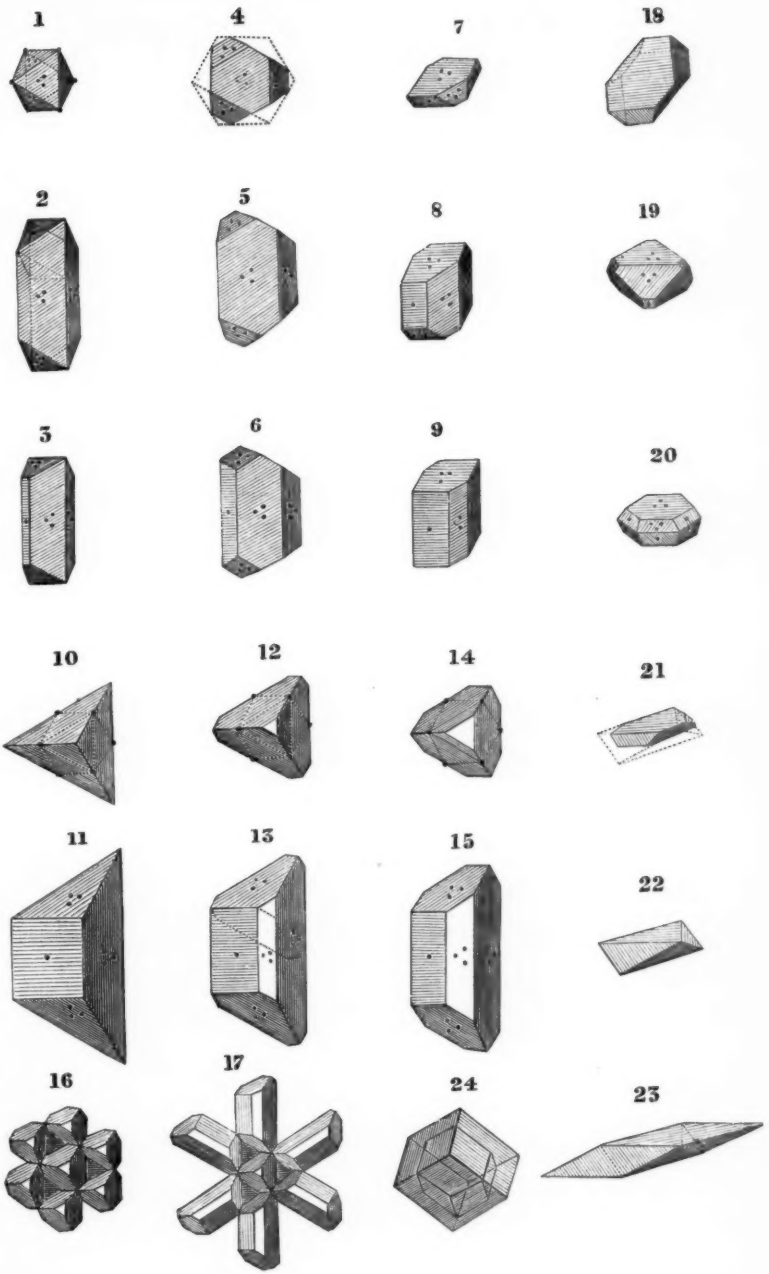



PLATE X.

# PLATE XI.


Fig. 7.
Fig. 3.
Fig. 8.
Fig. 5.
Fig. 4.
Fig. 6.
Fig. 2
Fig. 9.
Fig. 1.
Fig. 10.
Fig. 11.
Fig. 12.

# PLATE XII.



# PLATE XIII.

Fig 1.

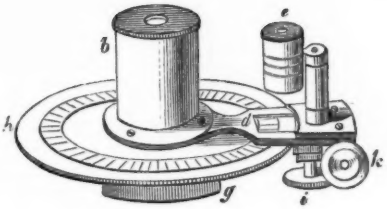



Fig 2.

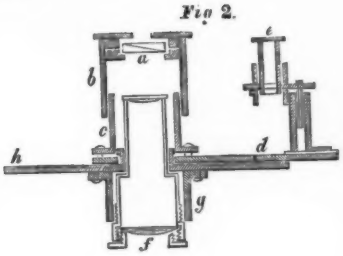



Fig. 3

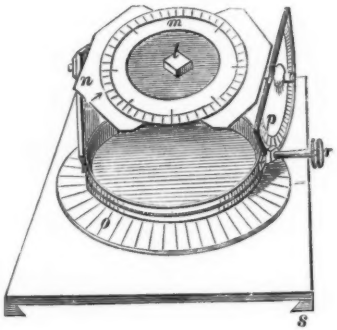



Fig. 4.

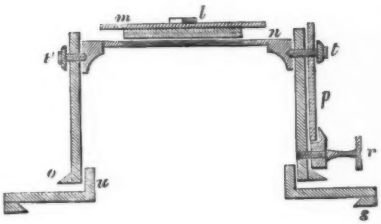



Fig. 5.

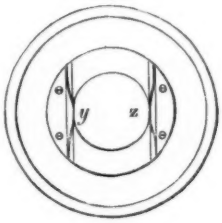



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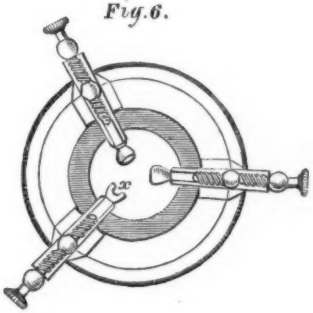



Fig. 7.

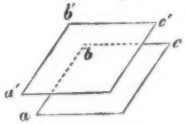



Fig. 8

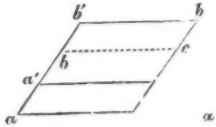



Fig. 9

